Boreskov Institute of Catalysis of Siberian Branch
of Russian Academy of Sciences, Russia

Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
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Chinese Academy of Sciences

Scientific Council on Catalysis of Russian Academy of Sciences,
Russia

Russian Catalytic Society

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3-d Russia-China Seminar on Catalysis

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ABSTRACTS
Part 2

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SEMINAR ORGANIZERS

- Boreskov Institute of Catalysis of Siberian Branch of Russian Academy of Science, Russia
- Dalian Institute of Chemical Physics, Chinese Academy of Science, China
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The Seminar program includes oral presentations (20 min) and posters in the following topics:

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PROPAGATION RATE AND WAVE STRUCTURE OF HETEROGENEOUS CATALYTIC COMBUSTION

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A distinctive feature of heterogeneous catalytic reaction is a peculiar coupling of chemical and transport processes in reactive system. That is why analysis of the reaction macro-phenomena (ignition, extinction, wave propagation) can provide useful information on chemical and physical kinetics of molecular processes.

The goal of this paper is to study the propagation mechanism of heterogeneous catalytic oxidation in a channel of porous material. A theoretical model proposed for this process uses the theory of critical phenomena of heterogeneous exothermic reactions on an equally accessible surface [1,2], as well as general theory of chemical wave propagation [3,4]. The model takes into account structural features of the porous material, and difference between the temperatures of material particles and filterable reacting gas. Emphasis is on the counter-flow propagation of the reaction wave in a channel. It is shown how the wave propagation rate correlates with the reaction constants and with the physical characteristics of the porous material and the reagent filtration. An explanation is offered for the effect of accelerated counter-flow propagation under filtration increasing [5]. The results are also used to explain the experimental data on transition dynamics of catalytic CO oxidation in the adiabatic packed bed reactor [6], and other experimental data on heterogeneous combustion.

Model of the process. A quasi-steady-state wave of heterogeneous reaction propagates with a rate u relatively to the channel surface. The reagent is filtrating with a constant velocity V. The distributions of reagent temperature Ò and concentration Y in the flow satisfy the one-dimensional equations of a heat-conductivity and diffusion (in a system of coordinates ($-\infty < x < +\infty$) associated with the wave):

$$(u+V)\,T'_x = (DT'_x)'_x + 4\beta(T_s - T)/d,\quad (u+V)Y'_x = (DY'_x)'_x - 4\beta(Y - Y_s)/d, \qquad (1)$$

The boundary values of reagent temperature and concentration at the entrance of channel ($x\to -\infty$, Ò = Ts = T_∞, Y = Y_∞.) are given, as well as the thermal equilibrium condition (dT/dx=0, dY/dx=0, Ts=T, Y=Ys) at the infinitely removed exit of channel ($x\to+\infty$). The index s corresponds to the values on the channel surface, d is the hydraulic diameter of a channel, β= NuD/d is a mass-transfer factor, D is a coefficient of reagent diffusion, Nu is the Nusselt's criterion. The diameter d can be estimated using the porosity Π and particle size r of a porous material. For example, in the case of model material consisting of rods having radius r, and filling a pipe in radius R, the diameter is equal: $d(r, R,) = 2\,rR / (r + (1-\Pi)\,R)$.

The rate of heterogeneous reaction F depends on Y_s and T_s according to the Arrenius law: $F_s = K_s Y_s^m$, $K_s = z \exp(-E/RT_s)$. The distributions Ts (x) and Ys (x) lead from the balance of mass and heat fluxes on the surface: $T_s = T_o' + q\beta(Y-Y_s)/(\alpha+\alpha_s)$, $Y_s^m = \beta(Y-Y_s)/K_s$, where To' is an effective temperature of the surface environment: $T_o'(x) = (\alpha T + \alpha_s T_o)/(\alpha + \alpha_s)$, $\alpha_s = \lambda s/d$, λs is the thermal conductivity of wall, q is the heat-release of the reaction. The critical conditions of reaction ignition (To')i =Ti (Y) and extinction $(To')_e = T_e(Y)$ are derived [1] as functions of the reaction constants and the transport coefficients. For example for the first order reaction (m=1), the critical conditions are: $(T^*-Ti)E/R(T^*)^2 = (1+\ln(y-2))$; $(Te-T^*)E/R(T^*)^2 = 2-y$, $(T^* = E/R\ln(z/\beta$, $y = \beta qYE/(\alpha + \alpha_s)R(T^*)^2)$.

A formula for the wave rate u is derived using the general theory of wave processes in nonlinear medium with dissipation [3,4]: $u = 4\,(D/d)[Nu(T_M-Ti)/(Ti - T_\infty)\,)]^{1/2} - V$. This formula specifies existence of the maximum of function u(V) observed in the experiments. An increase of u(V) is due (above all) to increase of the reagent concentration Y_o at the beginning of the reaction zone, and by increase of size of this zone.

Application of the analysis results to the catalytic CO oxidation in fixed-bed reactor [6] explains the critical regimes of reaction, characterized by temperature and concentrations pulsations.

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R&D ON SYNGAS CONVERSION IN GROUP 805 OF DICP

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The gas to liquid (GTL) techniques has being developed rapidly in the world due to the environmental protection requirements for the sustainable development of the economy. Developing of new technology of modified Fischer-Tropsch catalysts that allows to cut off the heavier end of the Schultz-Flory distribution is necessary. Under this strategic consideration DICP has commenced an R/D project for the one-step synthesis of synthetic fuel (major in diesel distillates) directly from syngas in 1990's. Based on our long-term works on Fischer-Tropsch synthesis, we have developed a novel selective F-T catalyst that produced synthetic fuel with major liquid phase product in the diesel fraction.

We have studied the effects of the cobalt promoter and the distribution of cobalt in the pores of the porous carrier on the activity and selectivity of the catalyst, especially on the effective suppression of the formation of methane and C_2–C_4 hydrocarbons by-products as well as the formation of heavier fraction, so as to optimize the production of diesel distillates in liquid oil-phase product.

Extensive studies have been reported to synthesize these C_2 oxygenates on rhodium based catalysts. However un-promoted rhodium catalyst produces mainly methane and the CO conversion is low, so various promoters have widely been employed to improve the performance of the Rh-based catalysts in the past decades. The Rh based catalysts promoted with oxide promoters, such as oxides of Fe, Mn, Zr, V, and La, are highly active and selective in formation of C_2 oxygenates. Rh-Mn-Li/SiO_2 catalyst is one of the most favorable catalytic systems for the effective synthesis of C_2 oxygenates. Recently, an iron promoted Rh-Mn-Li/SiO_2 catalyst, which showed superior activity in C_2 oxygenates synthesis, was developed in our group.

Hydroformylation is of high interest for both industry and academic science. Special methodologies for catalyst separation and recovery in the conversion of higher alkenes attract much attention. However, it has long been recognized that many homogeneous reactions are not commercially viable because of problems of catalyst recovery. Thus, significant efforts have been centered on the heterogenization of the organometallic species responsible for catalysis. We have explored an alternative approach, in which phosphines are directly employed to modify catalytic properties of highly dispersed metal heterogeneous catalysts through certain interaction between supported metal particles and phosphines. Here we show that this kind of catalysts exhibits high activity and selectivity, which are comparable to typical homogeneous catalysts for olefin hydroformylation. The difficulty of catalyst separation and noble metal recovery associated with the homogeneous catalysis can be prevented.

CATALYTIC PHOTOOXIDATION AND NUCLEATION OF PLANT-GENERATED GASEOUS COMPLEXES WITH HEAVY METALS

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Metal-containing compounds can be accumulated from soil by plants and released into the gas phase. This process is an important link in biogeochemical cycles of elements (Panichev, 1997). It involves the formation of volatile metal-containing compounds, either organometallic ones or complexes with organic ligands, terpenes being an example. The organic constituent originates from plants, while the metallic component gets into plant tissues from polluted soil. Keeping in mind extreme toxicity of heavy metals for humans, we investigated the mechanism by which these metals are transformed into the breathable fraction of submicron aerosol. We investigated cadmium- and zinc-containing compounds released by some herbaceous species, and revealed the catalytic action of metals and UV light on the oxidation of these compounds into metal-containing aerosol.

EXPERIMENTAL. To detect metal-containing compounds released by the plants, we added cadmium and zinc nitrates into the soil and planted small violets (the *Violaceae* family) and saxifrage (*Saxifraga effusa)*. Each plant species was investigated separately. The plants were placed in a cylindrical quartz tube through which a mixture of nitrogen and oxygen (4:1) was slowly blown. Samples of the gas phase and aerosol particles were collected at different distances from plants. A tube with a similar flowerpot containing cadmium- and zinc-enriched soil but without any plants in it was a blank. The total content of metals (a sum of metal concentration in the gas phase and in aerosol) was measured by sampling the air without any filters. To detect metals separately in gas an in aerosol, sampling through the aerosol filters into organic solvents was applied. The amounts of metals in gas and in aerosol phase were determined by means of mass spectrometry with inductively coupled plasma (ICP MS). The metal-containing compounds were identified with the help of high performance liquid chromatography using Milichrom-1 instrument with micro column filled with LiChrosorb. The UV absorption detector at 290 nm was used. After having identified the nature of organic ligands, we synthesized some of them specially to test their behaviour in the system in the absence of metals, to have a reliable reference point of their ability to be photo-oxidized.

RESULTS. We detected cadmium- and zinc-containing compounds in the gas phase in the vicinity of plants. It should be stressed that the formation of aerosol occurred only under irradiation; no particulate matter was detected in dark. No metals were present in the gas phase in the blank tube. We studied the dynamics of the oxidation of metal-containing gaseous compounds by oxygen. In the reference experiment, the organic component alone was subjected to photo-oxidation under the same conditions except for the presence of a metal. It was discovered that metal-containing compounds are volatile complexes of cadmium and zinc with alkylated derivatives of *L*-cysteine, *L*-glutamic acid and glycine, as well as substituted malates and citrates. The metal to ligand ratio in the volatile complexes was 1:2, which is an evidence of chelating, because coordination number typical for Cd^{2+} and Zn^{2+} is 4. Under irradiation with UV light in air, we sampled the freshly formed aerosol particles with the cellulose acetate filters and examined them by means of liquid chromatography and IR spectroscopy. Partial oxidation of the ligands was revealed: for example, the polyphenol fragment was transformed into the fragment of benzoic acid; coordination with metal ion was conserved. The rate of oxidation process was about 2 times higher with cadmium than with zinc. No changes in the oxidation state of Zn and Cd were detected, and the metals remained coordinated with the oxygen atom of ligand, but it was now the oxygen of carboxylic group instead of the phenolic OH in the initial volatile complex compound. In the experiment with organic components without metals, the oxidation was much slower and followed another route starting from the double C=C bonds and aldehyde groups HC=O of the organic ligands. A possible explanation of these changes in the process mechanism can be the catalyzing action of metal ions on the photooxidation of organic ligands. This mechanism can be actual under natural atmospheric conditions also for other heavy metals. It can be one of the sources of fine atmospheric metal-containing organic aerosol, especially in case of severe anthropogenic contamination of soil by heavy metals.

CONCLUSIONS. Photooxidation of cadmium- and zinc-containing complexes with organic ligands and their transformation into aerosol was investigated. Catalyzing effect of the metals was revealed. This mechanism can contribute into the formation of fine organic metal-containing aerosol in natural atmosphere and requires thorough investigation because of severe health-damaging properties of such a kind of aerosol.

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METATHESIS OF ETHYLENE AND 2-BUTYLENE TO PROPYLENE ON WO_3/HY-Al_2O_3 CATALYST *WITH* DIFFERENT g-Al_2O_3 *CONTENTS*

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Introduction

A wide variety of transition metal compounds catalyze the olefins metathesis and the most superior catalysts are those based on W, Mo and Re. In particular, rhenium-based catalysts attract much more attention because of their high activity and selectivity even at room temperature [1]. However, rhenium is a noble metal and catalysts with low rhenium loading have negligible activity [2]. W-based catalysts possessing good reaction performance become an alternative despite the higher reaction temperature than that for Mo and Re-based catalysts. ABB Lummus has reported a WO_3/SiO_2 catalyst for the metathesis of ethylene and 2-butene, which shows 2-butene conversion 65~70% and selectivity above 90% at 250~300°C [3]. In our experiment, we find a novel catalyst 3.0W/HY-30%Al_2O_3 catalyst, which possesses 2-butene conversion ca. 60% and propylene selectivity ca. 88% even at 180°C. In this article, we report the related interesting results.

Experimental

WO_3/HY-Al_2O_3 catalysts with 3.0 wt% tungsten loading were prepared by an impregnation method [4]. According to the weight ratio of γ-Al_2O_3, all these WO_3/HY-Al_2O_3 catalysts were denoted as 3.0W/HY-$X$$Al_2O_3$, X indicating the weight percents of γ-Al_2O_3 in the HY-Al_2O_3. These so-prepared catalysts were evaluated in a stainless fixed-bed flow reactor with an internal diameter of 10 mm at 180 °C. 3g of catalyst with an average particle size of 0.56-1.3 mm was employed. The catalysts were characterized by NH_3-TPD and BET techniques.

Results and discussion

Fig. 1 shows the influence of γ-Al_2O_3 content on the activity of 3.0W/HY – $X$$Al_2O_3$ catalysts. The initial activity of 3.0W/HY-$X$$Al_2O_3$ (TOS = 1h) increases remarkably with the increasing γ-Al_2O_3 content in the range of 0~10 wt%, then it reaches a plateau (~60%) between 10~70 wt%. After that plateau, the activity begins to decrease. The propylene selectivity and catalyst time of stable performance have the similar trends as shown in Fig 1. These results reveal that the combination of HY zeolite and γ-Al_2O_3 is prerequisite in order to obtain highly active catalysts for the metathesis of ethylene and 2-butene. NH_3-TPD and specific surface area data for the 3.0W/HY-$X$$Al_2O_3$ with different γ-Al_2O_3 contents were obtained. The total acidity and specific surface area decrease with the increase of γ-Al_2O_3 content. There seems to be no direct correlation of the reaction performance of 3.0W/HY-$X$$Al_2O_3$ with the above physico-chemical properties. The 3.0W/HY sample has major Bronsted acidity and minor Lewis acidity, while the 3.0W/γ-Al_2O_3 possesses only Lewis acidity. By changing the γ-Al_2O_3 content in the HY-Al_2O_3 from 0 to 100 wt%, the ratio of Bronsted acidity to Lewis acidity decreases, though we can not confirm the precise value by the pyridine-FTIR technique. According to the above results, the reaction performance may be controlled by the ratio of Bronsted to Lewis acid sites in the 3.0W/HY-XAl_2O_3 catalysts. There are some differences with the existing views, e.g. Xiaoding Xu has reported only a relation between activity and Bronsted acidity [5], and Commereuc et al. have proposed that the good processing of the metathesis is governed by the Lewis acidity [6]. Further work is still under way.

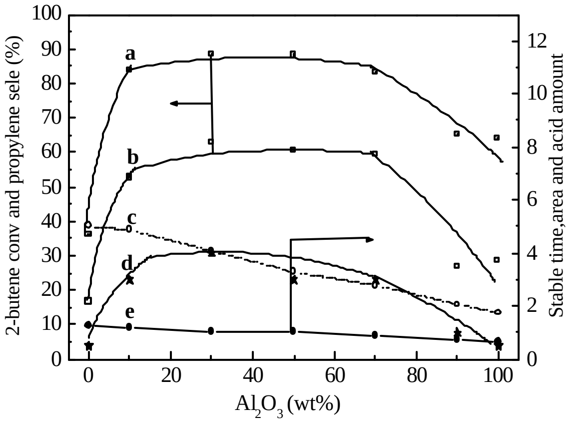

Fig. 1. (Left) Reaction performance and physico-chemical properties as a function of γ-Al_2O_3 content in the 3.0W/HY-xAl_2O_3 ; Reaction conditions: 180 °C; WHSV=1.5 h^{-1}; ethene/2-butene=1 (mol ratio); 0.1MPa
a: propylene selectivity (%);
b: 2-butene conversion (%);
c: surface area ($\times 10^2$ m^2/g);
d: time of stable performance (h);
e: total acid amount ($\times 10^{20}$)

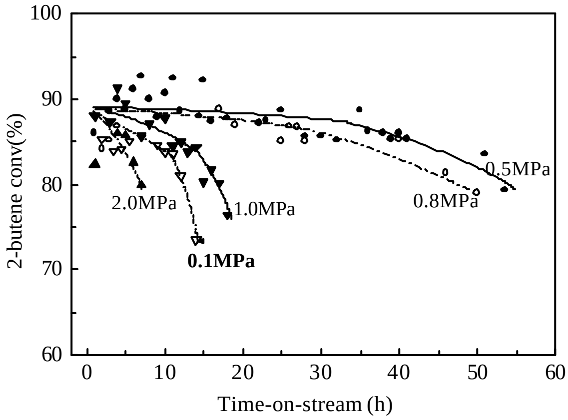

Fig. 2. (Right) 3.0W/HY-30Al_2O_3 catalytic performance under different pressures
Reaction condition: 180°C;
WHSV=0.83 h^{-1};
ethene/2-butene=3 (mol ratio)

At the end, effect of reaction temperature and space velocity on the reaction performance of the 3.0W/HY-30Al_2O_3 catalyst was investigated. Upon the increasing of the reaction temperature from 90 to 180 °C, the initial 2-butene conversion rises from 23.0% to 87.2%, which indicates that suitable temperature is favorable to activate 2-butene and ethylene. However, too high reaction temperature such as 210 °C results into quick deactivation owing to intensification of side reactions. With decreasing of space velocity the stability of catalyst increases. It is somewhat interesting that pressure effects the catalyst stability (Fig. 2). For this process ($CH_2=CH_2+CH_3CH=CHCH_3 \longrightarrow 2CH_3CH=CH_2$), reaction pressure should not influence the stability. However, the stability of catalyst decreases with the pressure changing from 0.5 to 2.0 MPa, and stability under 0.1MPa is rather low. This indicates that suitable pressure such as 0.5~0.8MPa are beneficial to keep the stability of catalysts.

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ONE – STAGE CATALYTIC CONVERSION OF HEAVY OIL FRACTION INTO THE PARAFFIN-GASOIL FRACTION

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The observed in last year deficit of resources and mining of light oils lead to intensification of development and searching of new ways of treating of high-boiling residue. It's known that the difficulties connected with catalytic destruction of fuel oil hydrocarbons are caused by the presence of sulfur-, nitrogen-containing compounds and heavy metals, which poisoned the used catalysts. Therefore the high-cost prerefining of the fuel oil from the harmful compounds is used.

The new technological scheme of oxidative catalytic cracking of fuel oil excludes this stage because of one-time using of cheap catalysts obtained from natural Kazakhstan's alumosilicates. Catalyst consumption in this method is 2 kg on 1 ton of raw material. The results of oxidative cracking of M-100-mark, Shymkent petroorgsynthesis plant (SPOP) and Pavlodar petrochemical plant (PPKP) fuel oils are shown in Table 1.

Table 1.

Fuel oil mark	Sulfur concentration in fuel oil, mas.%	The yield of cracking products, mas.%					
		Gas	Gasoil	Light gasoil	Heavy residue	Wastes	Total
M-100	0.5	0,8	1,1	85,7	12,7	0	100,0
SPOP	0.5	4,9	5,0	79,1	10,5	0,5	100,0
PPCP	2.7	1,4	1,1	75,5	21,6	0,4	100,0

The one-time using of catalyst excludes the stage of vapor treating and regeneration that decreases the power input and improves the ecology of the process. It's a low-waste process because of formation of small amount of gas hydrocarbons, and heavy residue with admixture of exhausted catalyst may be used in manufacturing of road covering. The productivity of the process is high enough if 0,2% suspension of fine dispersed catalyst in a fuel oil is poured into the flow reactor with the rate equal to the volume of the reactor in an hour. The volume rate of an air simultaneous feeding is not more than 0,15 h^{-1}. The temperature of catalytic cracking is 470-480 °C.

The results of investigation of the light gasoil, which was obtained as a result of M-100 and PPCP fuel oils cracking, are presented in Table 2.

Table 2.

The title of index	The index volume for light gasoil		
	On state standard 305-22 for summer mark	From M-100 fuel oil	From PPCP-fuel oil
The cetane number, not less than	45	56,4	49,3
Fraction composition:			
50% distils, not over than, °C	280	302	284
96% distils, not over than, °C	360	360	360
Kinematical viscous at 20°C, mm^2/s	3,0-6,0	5,04	4,01
Temperature of freezing, °C, not over than	–10	–12	–12
Temperature of turbiding, °C, not over than	–5	–2	–1
Temperature of flash, defined in closed tigle, °C, not lower than	40	<15	<15
The mass part of sulfur, %, not more	0,2	0,16	0,62
The mass part of mercantile sulfur, %, not more	0,01	0,01	0,02
The contents of H$_2$S	Absence	0,0035	0,0001
Acidity, mg KOH on 100 sm^3, not more than	5,0	5,42	4,22
The examination on copper flat	Pass	Don't pass	Don't pass
The concentration of fact resin, mg KOH on 100 g fuel, not more than	40,0	26,5	25,3
Iodine number, g I$_2$ on 100 g fuel	6	6,9	1,2
The filtering coefficient, not more	3	1,6	1,9
Ashes forming, %, not more	0,01	Absence	Absence
Cokeforming 10% of residue, %, not more	0,20	0,06	0,17
Water content	Absence	Absence	Absence
Density at 20°C, kg/m^3, not more	860	838,0	850,6

The investigated fuel oils differ by sulfur content and PPCP's fuel oils refer to highsulfur one (Table 1). In spite of that the fuel oils weren't desulfurized, the sulfur concentration in light gasoil formed during M-100 fuel oil cracking doesn't exceed the value stated by GOST for summer diesel fuel. It's cetane number is equal to 56,4 and corresponds to the index for elite sorts of diesel fuel. The light gasoil obtained by cracking of PPCP highsulfur fuel oil by sulfur contain exceed the standard value, but also has a high cetane number. For improving of its quality it is necessary to combine it with fraction of direct gong light gasoil for obtaining the diesel fuel corresponding to the standard.

PLUG-THROUGH CONTACTOR MEMBRANES (PCM) FOR THE FISCHER-TROPSCH SYNTHESIS

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What is wrong with the traditional reactor designs?

Fischer-Tropsch synthesis (FTS) is the complicated three-phase process of CO hydrogenation to hydrocarbons, which attracts the attention of research institutes and industrial companies. Specific features of the FTS make crucial the following requirements to the FTS reactor [1]:

(1) isothermal catalyst bed; (2) high concentration of the catalytically active substance in the reactor volume; (3) high gas-liquid interface surface area; (4) small effective size of catalyst grains (i.e. small effective diffusion length); (5) low pressure drop; (6) low water concentration (e.g. low backmixing in the reactor volume).

These requirements seem to be common for any Fischer-Tropsch process with no concern about the raw material source or product market.

The traditionally used slurry bed reactor designs satisfy the demands 1) and 3)-5), however the catalyst concentration in the reactor volume is rather low due to the conflict between the loading of a particulate matter in the slurry and the effective dynamic viscosity of the latter, which promotes coalescence of gas bubbles and a decrease in gas hold-up in the slurry. The interphase mass-transfer in the bubble slurry reactors diminishes strongly when the catalyst loading is above 20-25 vol.%. As a result, the space-time yield of hydrocarbons is low and the dimensions of industrial apparatuses are huge: the SASOL Slurry Phase Distillate (SPD) reactor with productivity of 2500 barrels per day has 22 m in height and 5 m in diameter [2].

In circulating fluidized bed (CFB) reactors [3] the catalyst concentration in the reactor volume is of the same value. However, the construction of the reactor is much more complicated and the prevalent part of the catalyst is stored in the loading hopper.

The fixed catalyst bed is more dense, but the conflict between the reasonable hydraulic resistance (large catalyst grains needed) and low diffusion constrains (small catalyst grains needed) results in even worse process performance. This contraposition can be resolved using the "egg-shell" catalysts [4] with, however, a low concentration of the active component in respect to the entire particle volume.

Recently, the solution of the knotty problem of trade between high concentration of the active component and diffusion limitations was suggested by using the heat-conductive plug-through contactor membranes (PCM).

What are the PCM membranes?

The PCM is a three-component mixture of a catalytically active substance, pore-producing agent and reinforcing agent with a high heat conductivity, which is sintered and reduced in H_2 after mixing [5]. Finally, the PCM is a three-modal porous structure, which is permeated by the syngas (see Fig. 1). The pores with the effective radius above 2-3 μm are almost gas-filled and are responsible for the gas permeation. The smaller pores are flooded with liquid products due to capillary forces and are not permeable. The most narrow pores (effective radius less than 0.5 μm) are located inside the catalyst particles and the mass transfer within these pores is accounted for by the molecular diffusion.

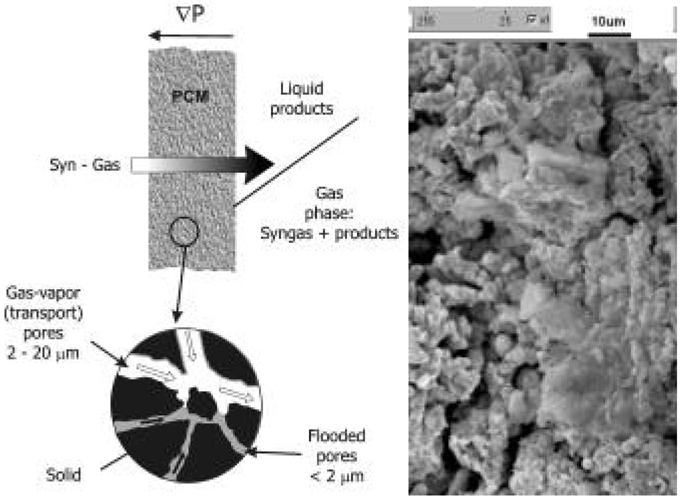

Fig. 1. The scheme of the Fischer-Tropsch synthesis in the PCM membrane reactor and the SEM image of the PCM.

PCM can combine high permeability (above 20 mDarcy), high mechanical strength (above 20 kg cm^{-2}) and high heat-conductivity (above 4 W(m K)$^{-1}$). Therefore, it provides low pressure drop and isothermicity. At that the intense convective mass-transfer within transport pores, high specific area of these pores (which can be roughly considered as the specific gas-liquid interface area) and small distance between two adjacent transport pores (which is a good estimation for the effective diffusion length) weaken the mass-transfer constrains. This allows to achieve high space time yield of hydrocarbons (60-70 kg (m^3 hr)$^{-1}$ at 0.1 MPa, 210 °C and 150-200 kg (m^3 hr)$^{-1}$ at 2.1 MPa, 210 °C) and high selectivity towards heavy hydrocarbons ($\alpha > 0.85$) and olefins (propene:propane ratio of 6-10).

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STABILIZATION OF TETRAHEDRAL Co^{2+} AND Cu^{2+} IONS BY EXTRALATTICE ALUMINIUM ATOMS IN THE CHANNELS OF HZSM-5 ZEOLITE

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The present study deals with HZSM-5 zeolite with Co^{2+} ions incorporated therein. The tetrahedral Co^{2+} ions have been shown to stabilize in the channels of the HZSM-5 zeolite through interaction with extralattice aluminium atoms. Commercial HZSM-5 zeolite (Si/Al=17) has been used to synthesize CoZSM-5 zeolites. Cobalt has been introduced into the zeolite channels by incipient wetness impregnation using an aqueous $CoCl_2$ solution followed by the treatment with a diluted ammonia solution at pH=9. Two samples have been prepared containing 2.0 and 5.0 wt. % of Co^{2+} (Co(2)ZSM-5 and Co(5) ZSM-5, respectively).

In the UV-VIS-spectra obtained for the Co(2)ZSM-5 and Co(5)ZSM-5 samples dried at 110°C, adsorption bands (a.b.) at 16500 cm^{-1} assigned to the $^4A_2(F)$–$^4T_1(P)$ transition of Co^{2+}_{Td} ions and at 17600 cm^{-1} - to Co^{2+}_{Oh} ions are observed. The band at 16500 cm^{-1} of Co^{2+}_{Td} ions shifts to 15200-15600 cm^{-1} after calcinations of CoZSM-5 at 450°C. Hence,Co^{2+}_{Td} ions are stabilized in a close to ideal tetrahedral oxygen coordination. Note, that an increase of the calcination temperature shifts a.b. at 17600 cm^{-1} of theCo^{2+}_{Oh} ions only slightly.

FTIR spectra of the initial zeolite comprise bands at 3665, 3702 and 3784 cm^{-1} that correspond to AlOH-groups located on extralattice aluminium atoms. A band at 3612 cm^{-1} assigned to structural OH-groups located in the zeolite lattice also is observed. The inspection of IR-spectra of adsorbed CO reveals extralattice Al^{3+} (mainly in the form of a multinuclear hydroxocomplexes: a.b. at 2229, 2220 cm^{-1}) and an oxide-alumina cluster (a.b. at 2187, 2197 cm^{-1}) in the channels of the initial HZSM-5 zeolite. The cobalt ions introduced into the zeolite channels interact with both structural OH-groups and extralattice aluminium. Notice that the bands of CO adsorbed on extralattice Al^{3+} disappear upon introduction of cobalt in the zeolite but intensive bands 2207 and 2193 cm^{-1} appear instead, the former corresponding to isolated Co^{2+} ions and the latter to associated Co^{2+} ions. It is shown that the concentration of the cobalt associates increases with the content of Co^{2+}. These results agree well with the UV-VIS data.

To assure in a correct interpreting the UV-VIS spectra, we have synthesized a sample of well crystallized $CoAl_2O_4$. In the UV-VIS-spectrum of this sample, almost resolved multiplet bands are observed at 16000 and 17200 cm^{-1} ($Co^{2+}{}_{Td}$ ions) and at 18400 cm^{-1} ($Co^{2+}{}_{Oh}$ ions). The UV-VIS spectra of calcined Co-ZSM-5 and $CoAl_2O_4$ are seen to be similar to each other.

From the data obtained, the tetrahedral stabilization of Co^{2+} ions in the channels of HZSM-5 zeolite is assumed to be possible only due to an interaction with the extralattice aluminium. Seemingly, one-dimensional $CoAl_2O_4$ nano-analogues are formed in the zeolite channels during the synthesis and heat treatment.

The discovery of Co^{2+} ions stabilization in the HZSM-5 zeolite channels due to an interaction with extralattice aluminium that results in the formation of one-dimensional $CoAl_2O_4$ nano-analogues is important for understanding how double-charged cations are stabilized in different systems, e.g. in CuZSM-5 zeolite. The stabilization of Cu^{2+} ions with tetrahedral coordination in channels of CuZSM-5 zeolite is supposed [1] on the basis of a.b. 6100 cm^{-1} and 22500 cm^{-1} in the UV-VIS spectra. The latter band is assigned to the ligand-metal CTB of $[Cu^{+}–O–Cu^{2+}]$ complexes [1]. In our opinion, it is necessary to consider the a.b. 6100 cm^{-1} together with 22500 cm^{-1}. If so, they can be ascribed to a d-d transition and a ligand-metal CTB of the $Cu^{2+}{}_{Td}$ ions in $CuAl_2O_4$ formed due to the interaction of copper with extralattice aluminium in zeolite channels. This assumption is most probable for zeolite with low ratio Si/Al~12 [1]. $CuAl_2O_4$ contains the $Cu^{2+}{}_{Td}$ ions. The deliberately synthesized $CuAl_2O_4$ gives a.b. at 6200 and 7300 cm^{-1} due to the d-d-transition (E_g–T_{2g}) of Cu^{2+} ions in a weakly distorted tetrahedral coordination, and the related ligand-metal CTB at 22500 cm^{-1}. The results obtained and the literature data demonstrate that the observed tetrahedral stabilization of Cu^{2+} ions inside the HZSM-5 zeolite channels [1] is possible only due to the interaction of double-charged cations with extralattice aluminium to produce $CuAl_2O_4$ during the synthesis and the following thermal treatment. Therefore, anyone who synthesizes M^{2+}ZSM-5 should take into account the possibility of the interaction of M^{2+} ions with extralattice aluminium localized in HZSM-5 channels.

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CATALYTIC CONVERSION OF METHANE IN REACTIONS WITH CARBON TETRACHLORIDE

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Since methane is undoubtedly one of the most inert organic compounds, the scope of methods allowing the conversion of CH_4 into commercially important chemicals is strictly limited. In this work a novel method of using CH_4 in organic synthesis based on catalytic reactions with carbon tetrachloride was proposed. We found that in the presence of catalysts CH_4 reacts smoothly with CCl_4 to give mainly perchloroethylene widely used as an efficient solvent in chemical purification. The process is described by the following equation: $2CCl_4 + 2CH_4 \rightarrow C_2Cl_4 + 2HCl + 2CH_3Cl$.

The method proposed herein has some advantages as compared with conventional processing. Firstly, the use of such inexpensive and readily available raw materials as CH_4 and CCl_4, the latter being a by-product of some technological processes (e. g. manufacturing of CH_3Cl and $CHCl_3$), makes the technological process cost-efficient. Secondly, compared with known methods of producing C_2Cl_4, the method proposed allows reducing the amount of toxic polychlorinated wastes as well as utilizing of ñhlorine not involved in the formation of C_2Cl_4 to obtain useful chemicals ($CHCl_3$ and CH_3Cl). Moreover, the process proposed makes it possible to inhibit the formation of gaseous HCl which could not be properly utilized. Finally, by employing transition metal compounds for initiating radical-chain reactions the process could be efficiently conducted under relatively mild conditions (250-400°C).

While testing the above method on a laboratory flow-type apparatus, an excellent level (80-95%) of both CCl_4 conversion and useful products selectivity was achieved. In addition, the amount of wastes was reduced to 1-3 %. The conditions (temperature regime, ratio of reagents applied, content of active component in catalyst) affecting the yield and C_2Cl_4 selectivity were also investigated. It was demonstrated that by increasing both the contact time and temperature the increase in CCl_4 conversion and C_2Cl_4 selectivity was achieved. Significant decrease in the yield of converting CCl_4 was observed at temperature below 250°C whereas at high temperature (above 400°C) coal-like precipitations on the surface of catalyst were formed thus reducing its activity. Optimal conditions of the process were determined allowing the achievement of converting CCl_4 up to 95% and high selectivity of forming perchloroethylene. Step-by-step scheme of CCl_4 interaction with CH_4 on catalysts containing transition metal compounds is also proposed.

IR STUDY OF ACTIVE SITES OF HIGH- SILICA PROMOTED ZEOLITE CATALYSTS OF LIGHT ALKANES AROMATIZATION REACTION

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Dehydrocyclization (or aromatization) reaction over high silica zeolite based catalysts is well known as light alkanes upgrading process [1]. Zeolites of ZSM-5 structure (SiO_2/Al_2O_3= 40) promoted with Zn and Cr ions were studied in this work. This catalyst demonstrates a high efficiency in BTX (benzene, toluene, xylenes and others alkyl aromatics) formation via propane-butane mixture aromatization [2]. Zn and Cr ions promoting effect was detected (Fig. 1).

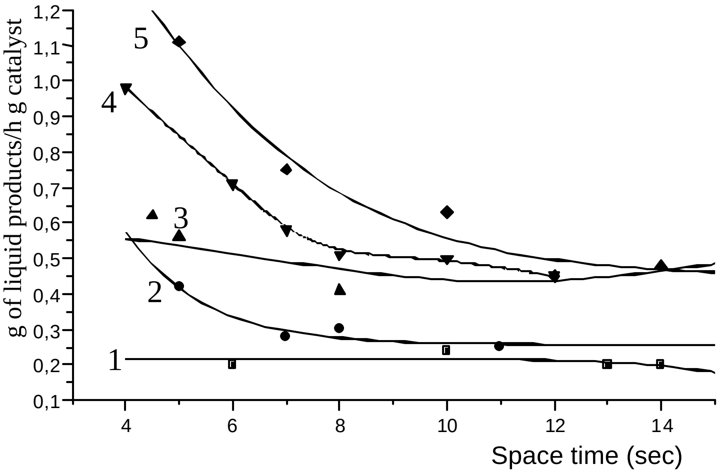

Fig. 1. The effect of time on the liquid products formation (t=600-610°C) from propane (75%) – butane mixture for the catalysts studied:

1 – non- promoted;
2 – 1%Cr promoted;
3 – 1% Zn promoted;
4 – 2% Zn promoted;
5 – 1% Zn+1%Cr promoted.

The present work deals with the infrared spectroscopy (IRS) study of proton donor (B) and electron acceptor (L) acidic sites of zeolite catalysts denoted in Fig. 1 legend. B-sites were directly investigated by infrared spectroscopy (IRS) by the OH group stretching vibration (Table 1). The band shift resulting from the formation of hydrogen-bonded complexes of OH group with benzene characterized acid strength. IR identification of L-sites was performed indirectly using the adsorption of CO test molecule. IR spectra were recorded

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at room temperature with EQUINOX 55/S (Bruker) FTIR spectrometer. 0.25-0.5 mm catalyst powders were placed in a quartz cell with CaF_2 windows. The samples were preheated at 600 °C for 2 h in air and for 2 h in vacuo (10^{-4} Torr).

FTIR spectra of the B sites (Table 1) comprise bands assigned to strongly acidic Si(OH)Al bridging groups, moderate acidic Al(OH) or probably promoter (OH) groups located on extralattice ions, and weekly acidic silanol group.

Table 1. B- sites IRS characterization (ν,cm^{-1}; PA, kJ/mol)*/

Promoter	Si(OH)Al bridging		Al(OH) or promoter(OH)		Si(OH)	
	ν	PA**/	ν	PA	ν	PA
no	3612	1160	3663	1200	3745	1350
1%Zn	3612	1150	3662	1200	3745	1340
1%Cr	3612		3660	1260	3745	1340
2%Zn	3614(3612)	(1240)	3661(3660)	1300(1300)	3745(3745)	(1340)
1%Zn +1%Cr	no		3675 (3653;3672)	1240-1280 (1290;1270)	3475(3745)	1350 (1360)

*/In brackets- after reaction- regeneration cycle.
**/PA- proton affinity value, calculated as $PA^{OH}= \{PA^{SiOH} -(1/0,00226)\ lg(\Delta\nu_{OH}/\Delta\nu_{OH}^{SiO2})\}$ ±25 kJ/mol, where PA^{SiOH}= 1390 kJ/mol, $\Delta\nu_{OH}^{SiO2}(C_6H_6)$ =110 cm^{-1} [3]

Table 1 data indicates a disappearance of Si(OH)Al band in 1%Zn +1%Cr promoted sample. Some differences in characteristics of OH groups attached to extra lattice metal ions are also observed. We ascribe these differences to formation of a new B-centers, which can affect catalytic activity.

IR-spectra of adsorbed CO (Table 2) reveal a differences in absorption peaks position and intensities of promoted and non-promoted catalysts. Suppositions may be made that differences observed correspond to a nature and concentration of L-sites.

Table 2. L- sites IRS characterization using adsorption of CO

Promoter	Types of sites interacted with CO (ν, cm^{-1})			
	B- sites	Extralattice Al^{3+}	Extralattice Al^{3+}, promoters, lattice L- sites	
no	2168	2193	2213	
1%Zn	2176	2193		2220, 2229
1%Cr	2173	2189		2219, 2229
2%Zn	2175	2193		2221,2230
1%Zn +1%Cr	2175	2187	2212	2220

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PALLADINIZED POROUS POLYPROPYLENE HOLLOW FIBER MEMBRANES FOR HYDROGENATION OF DISSOLVED OXYGEN IN WATER

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Dissolved oxygen is one of the major contaminant in the production of ultra-pure water. For the removal of oxygen to very low levels (less than 1 ppb for semiconductor industry), a catalytic reduction with hydrogen is an attractive method. Membrane reactors for hydrogenation processes based on supported palladium were investigated for similar processes, e.g. hydrogenation of nitrate in water [1]. So far, a catalytic non-permselective membrane reactor (CNMR) concept has been explored. In the CNMR hydrogen and water are supplied on opposite sides of a hydrophilic porous inorganic membrane. The catalyst is placed on the pore walls of the fine layer. Due to the capillary forces the liquid is sucked into the pores and stopped at the point where capillary pressure is equaled by the pressure difference between the gas side and the liquid side. Therefore, to provide a good control of the location of the phase boundary a uniform pore size of the fine layer is needed.

To overcome these problems the long-term objective of this work is to develop a hydrophobic low-temperature catalytic membrane contactor/reactor for hydrogenation. To this end, the following has been explored in this work:

i) the integration of the catalyst phase with a hydrophobic porous polymeric membrane that keeps water on the membrane external surface;

ii) the catalyst is present only at the solid/liquid interface where the reaction takes place and

iii) hydrogen is added on the inside of the hollow fibre membrane. This system is expected to minimize mass transfer resistances, resulting in optimal performance and minimal required membrane surface area and amount of catalyst.

The base membranes used were Accurel polypropylene (PP) hollow fibers from Membrana (Accurel Q3/2 and Accurel PP 50/280). Two methods of chemical deposition of Pd onto PP hollow fiber surface were used: i) reduction of tetraamminepalladium chloride by hydrazine hydrate (method I) and ii) reduction of palladium chloride by aliphatic alcohol (method II). The virgin membranes, Pd thin layers and catalytically active membranes were characterized by gas permeation and bubble point testing, by EXAFS, ESCA, XRD and SEM. It was shown that palladinized PP porous hollow fiber membranes kept hydrophobicity and porosity on the level of initial PP membranes. Catalytic membrane reactor tests proved that the developed palladinized hollow fiber membranes reduced effectively the dissolved oxygen content in water.

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SCIENTIFIC BACKGROUNDS AND ENGINEERING LAYOUT OF THE CATALYTIC PROCESSES OF OLEFIN CONVERSION DEVELOPED IN IPCP RAS

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For the last decades at least 50 weight % of all synthetic products have being obtained from ethylene and other olefins. That is why the problems of production and conversion of these monomers take the central place in the investigations and developments of the IPCP RAS.

The scientific backgrounds of the processes of controlled ethylene polymerization with the use of the original mono- and bi-centered, as well as mono- and bifunctional organometallic, metallocene and post-metallocene complex catalysts have been developed in the IPCP RAS over the last 20 years. The term "controlled polymerization" means the chain processes of ethylene and other olefins conversion having polymerization nature, which provide the efficient regulation of the molecular-mass distribution, of the chain branching, of the products functionality, as well as the total efficiency and selectivity of these processes. The properties of the products obtained in these processes are strongly depended on the material chain length.

The fundamental investigations and technological development, which have been fulfilled at the pilot continuous plant in the ICPC RAS, led to development of scientific backgrounds and engineering layout of the production of butene-1, hexadiene-1,4, higher linear alpha-olefins C4-C30, waxlike polyethylene, higher mono- and polyalkylaromatic hydrocarbons, olygomeric bases of unsaturated, hydrogenated, and aromatic oils of various applications, as well as of synthetic polyethylene composition materials. Some of them have already been commercialized. A number of the other processes are at the different stages of elaboration now.

The results of the elaboration of the catalysts and the influence of various factors on the kinetic peculiarities of the olefin consumption upon the regulated polymerization; on the structure, molecular-mass distribution and some other characteristics of the products; on the selectivity of the most advanced of the above-mentioned processes will be presented in the report. The mechanisms of these processes will be discussed. Also the results of the investigation of the radical stages in the CMC and MCC (complex organometallic and metallocene catalysts) reactions and their role in the polymerization processes will be reviewed.

In the final part of the report, the results of the technological design of given processes will be presented.

EXPERIMENTAL STUDY, MATHEMATICAL MODELLING AND BASIC ENGINEERING OF THE PROCESS OF SYNGAS CONVERSION INTO GASOLINE OVER ZnO-Cr_2O_3/HZSM-5 CATALYST

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Many research groups around the world have made significant efforts to the development of a process for the production of gasoline from natural gas via synthesis gas formation. During the recent decades, various industrial multi-stage versions of synthesis gas transformation to gasoline have been proposed such as the MTG process of Mobil (three-stage process) and the TIGAS integrated gasoline synthesis process of Haldor-Topsoe, which incorporated a combined methanol and dimethyl ether synthesis with the MTG process.

An alternative route for the production of gasoline from syngas is a process on the ZnO-Cr_2O_3/HZSM-5 bifunctional catalysts, which allows combining several chemical reactions – methanol and dimethyl ether syntheses and their conversion to liquid hydrocarbons (gasoline range) – in a single reactor [1-4]. It was observed that the coexistence of the listed reactions on the “single” particle of bifunctional catalyst removes the thermodynamic equilibrium limitations for methanol synthesis favouring the overall syngas transformation to gasoline.

The subject of this report is experimental and theoretical studying of the effect of technological parameters of the process on the catalyst selectivity and productivity with regard to liquid hydrocarbons.

ZSM-5 zeolite was prepared via hydrothermal synthesis. To prepare the bifunctional catalysts, the powders of both zeolite and oxidic components were homogenised in a mortar in the desired proportion followed by pressing, crushing and sieving. The particle fractions of 0.25-0.5 mm and of 3-4 mm were used in the reaction.

The process of synthesis gas conversion to hydrocarbons was investigated on the laboratory and pilot installations in the temperature range 320 – 440°C, at pressures 40 - 80 atm, GHSV = 500 - 20000 h^{-1}, H_2/CO molar ratio = 2 - 10.

Results of bifunctional catalysts pilot testing are shown in the Table below. It should be noted that although aromatics content in C_{5+} hydrocarbons changed with temperature or H_2/CO ratio, all the gasoline fractions obtained had a low content of benzene (<1 wt.%). This fact is explained by the high alkylating ability of the acid component of the ZnO-Cr_2O_3/HZSM-5 catalysts [5]. It has been shown that the products distribution depends mainly upon the H_2/CO molar ratio and GHSV while the main factors affecting the process productivity are pressure and temperature in the reactor.

Table. Main results of bifunctional catalysts pilot testing

Reactor type, catalyst volume, L	Run duration, hr	Intervals of C_{5+} hydrocarbon distribution, % mass.				Octane Number of gasoline
		Iso-paraffins	Arom.	Olefins	Naphthene	
Adiabatic fixed bed, 2,8÷5,6	2000	75-85	3-15	3-4	1-3	80-82 MON
Isothermal fixed bed, 0,1÷0,5	120-500	50-80	15-45	1-3	3-5	85-93 RON

Kinetic modelling of the process of syngas conversion to liquid hydrocarbons on the basis of the experimental data obtained on ZnO-Cr_2O_3/HZSM-5 catalysts in a laboratory isothermal flow reactor has been carried out.

Mathematical modelling has been performed for the process flow sheet with the unreacted gas recycled. To simulate the process of hydrocarbons synthesis in a fixed-bed reactor, the one-dimension plug flow model was taken. To calculate the gas-liquid balance in the separator, we used a program based on the Gibbs energy minimization technique for the reaction components.

Basing on the experimental data and results of the mathematical modelling, technological calculations were performed for various versions of the reactor unit for industrial production of high-octane gasoline from synthesis gas. The obtained factors of expenditures and metal consumption of equipment were compared and the optimal version of the reactor unit was chosen. Basic engineering was developed for gasoline production installation of capacity 20 000 ton/year with respect to the desired product.

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THE REACTIVITY OF SULFUR FOR CATALYTIC PYROLYSIS OF PROPANE

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The interest to studies of interaction between sulfur and alkanes is provoked by a possibility of synthesizing a number of industrially valuable products. Among the products are CS_2, butadiene, thiophene and its homologues. Of particular interest is the development of processes for selective synthesis of olefins.

Potentially, molecular sulfur is a milder dehydrating agent in comparison with molecular oxygen; it seems realistic to provide a quantitative olefin yield through the reaction of alkanes with sulfur. The cyclic S_8 molecule is low reactive, its activation needs destruction of the cycle. Sulfur molecules containing less than eight sulfur atoms are more reactive. Thermal decomposition of S_8 molecules to produce low-molecular S_2–S_8 species is achieved at temperatures above 300°C [1]. The S_8 ring also can be opened in the presence of catalysts of the acid-base type or the ones containing transition metal ions, much more reactive surface-linked polysulfide chains being formed [2].

The present study is aimed at the study of the reaction of interaction between propane and sulfur vapor to yield olefins (C_3H_6 and C_2H_4) and H_2S at the ratio $C_3H_8/S\approx2$ in temperature range between 400 and 800°C. The variable parameters are contact time (0.5 to 5s) and propane concentration in the initial reaction mixture (10 to 50 vol %).

The studies of the influence of temperature and reaction mixture composition on the selectivity to propylene have shown that the rate of catalytic S-dehydrogenation of propane is high enough at the temperature not lower than 450°C. In the excess of propane, dehydrogenation is the dominant reaction at 450°C. The yield of hydrogen sulfide is close to 100% under these conditions. Organosulfur compounds (CS_2, CH_3SH, thiophene and dimethylthiophene) and cracking products (CH_4, C_2H_4) are not detected among the reaction products. At the same time, the yield of C_3H_6 is much lower (in two and more times). In the mentioned temperature range, the propane conversion decreases in the course of the reaction over all the catalysts under study. It is shown (by introducing propylene into the reaction mixture) that the side reaction of propylene oligomerization or condensation [1] results in a decrease in the selectivity to propylene during the S-dehydrogenation and in the catalyst poisoning caused by deposition of heavy products on the surface.

The temperature elevation to 550°C allows the propylene yield to be improved.

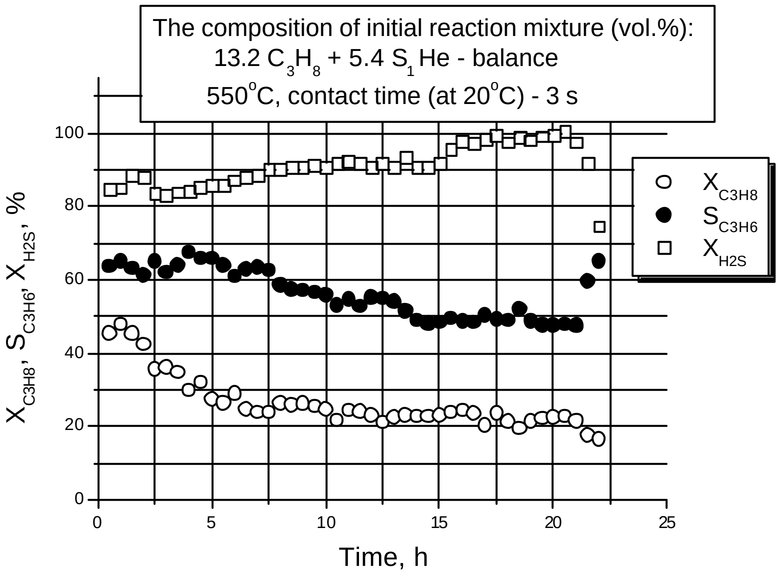

Fig. 1. Dynamic curves of conversion of C_3H_8 (X_{C3H8}), conversion of H_2S (X_{H2S}) and selectivity for C_3H_6 (S_{C3H6}).

However, the selectivity to C_3H_6 appears to be lower than the selectivity to H_2S. It is demonstrated (Fig. 1) that this is a continuous process for a long period of time (21 hours). The catalyst of the process under study is more advantageous than the ones for catalytic cracking of propane requiring regeneration as soon as after several minutes of operation. There are practically no cracking products (CH_4, C_2H_4). Decrease of the activity and selectivity is observed during first 5 to 8 hours of operation but not after X_{C3H8} became equal to ca. 25% and S_{C3H6} to 60–50%. The catalyst regeneration results in practically regaining of the process parameters during repeated reaction cycles.

Composition of the propane conversion products changes upon temperature elevation to 700 – 800°C. The equilibrium oligomer concentrations become negligible. As a result, the propylene fraction in the reaction products increases. However, the propane cracking following the equation $CH_3{-}CH_2{-}CH_3 \rightarrow CH_4 + CH_2{=}CH_2$ becomes perceptible at these temperatures.

The results obtained at 750°C and high concentrations of propane and sulfur demonstrate attainability of high concentrations of propylene (16 vol %) in the reaction products at high conversion of propane (75÷90%) (Figs. 2, 3).

The process is stable during 14-hour testing until the pipes and valves of the reactor system are blocked with heavy reaction products. As a result, the pressure in the system increases and the process has to be stopped. After the catalyst is regenerated in air and reaction deposits are removed from the pipes and valves, the process is resumed and the results of test cycle I are practically reproducible.

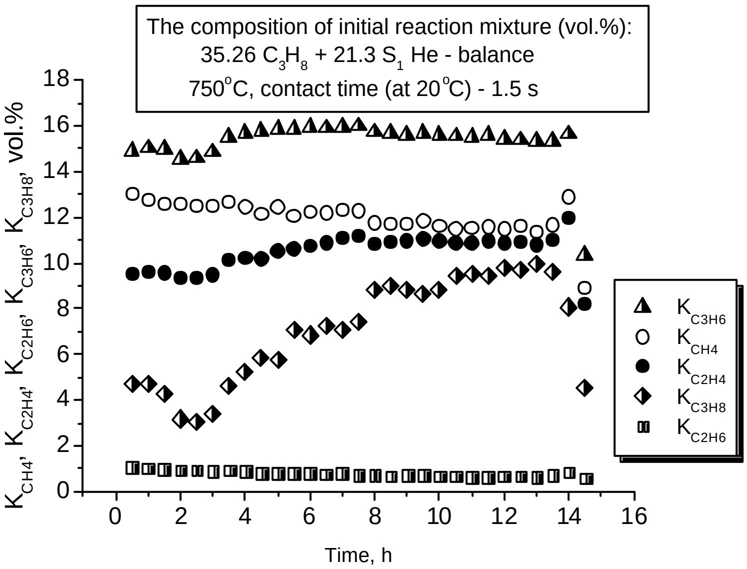

Fig. 2. Concentrations of CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 among the reaction products.

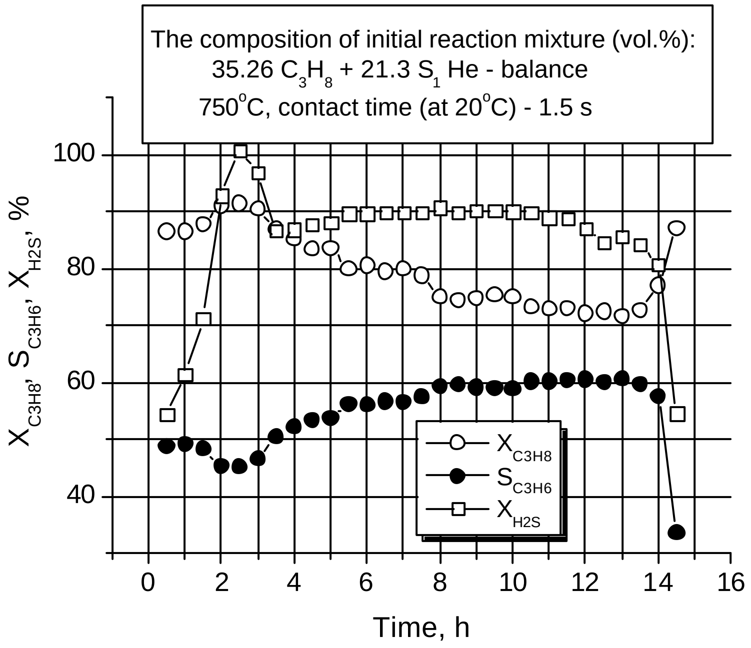

Fig. 3. Dynamic curves of conversion of C_3H_8 (X_{C3H8}), conversion of H_2S (X_{H2S}) and selectivity for C_3H_6 (S_{C3H6})

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CORUNDUM SUPPORTED MIXED OXIDES CONTAINING Ni AND Pt: ACTIVITY IN STEAM/DRY REFORMING AND PARTIAL OXIDATION OF METHANE INTO SYNGAS

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The catalytic partial oxidation of methane (CPO) to syngas is presently considered as an attractive technology for the small-scale and distributed production of CO and H_2 in the stationary and mobile fuel processing [1, 2]. In view of such applications, CPO could be realized at short contact times (< 0.1 sec.) and high temperatures close to 1000°C by running the process adiabatically [3]. Under these severe operating conditions, the determination of activity are complicated due to heat and mass transfer limitations as well as homogeneous gas-phase reactions. Thus, the problem on the nature of the CPO reaction pathway (whether the direct one in which CO and H_2 are primary reaction products or the indirect route proceeding via combustion of a part of CH_4 to CO_2 and water followed by subsequent steam (SR) and dry reforming (DR) of remaining CH_4) leading to syngas formation is still open.

Corundum supported catalysts comprised of lanthanum nickelate promoted by Pt and Ce-Zr oxide with a high bulk/surface oxygen mobility were shown to be active and stable in POM [4]. In this work, to elucidate the role of each catalyst component in POM proceeding via one or other route, POM activity of Pt, Ni, $LaNiO_3$ with and without Pt supported on two types of corundum either pure or promoted with CeO_2-ZrO_2 as well as their activity in dry and steam reforming were studied.

To prepare the catalysts, microspheric α-Al_2O_3 (100 μm diameter) containing 10% θ-Al_2O_3 (designated α,θ-Al_2O_3) or pure α-Al_2O_3 (0.2-0.25 mm fraction) were impregnated with necessary salt solutions followed by drying and calcination at 900°C. The catalysts were characterized by XRD and H_2-TPR. The catalyst were tested at atmospheric pressure in CPO (a plug-flow reactor, 900 ^{o}C, contact time 0.002 s, reaction mixture 1 vol. %. CH_4, 0.5 vol. % O_2 in He) and methane steam/dry reforming using a batch-flow installation at 750-850^{o}C and 5-20 l/h feed (contact time 0.14 - 0.036 sec) with $H_2O(CO_2) : CH_4$ ratios equal to 1.

Reducibility of the active components was found to depend on their composition as well as on the nature of a support. Thus, for active components supported on α,θ-Al_2O_3, TPR peaks are shifted to higher temperatures due to stronger interaction with θ-alumina admixture.

The activity of reduced catalysts in steam and dry reforming characterized by the effective rate constant depends on both the support nature and the active component composition (Fig. 1). All catalysts supported on pure α-Al_2O_3 possess a high activity in both reforming reactions. Furthermore, these catalysts are more active as compared with those supported on α,θ-Al_2O_3. A higher activity of former samples can be due to their easier reduction revealed by H_2-TPR. Among catalysts supported on α,θ-Al_2O_3, the highest activity is observed for complex active component containing Pt-promoted $LaNiO_3$ supported onto Ce-Zr oxide. According to TPR data, Ce-Zr oxide modifies the interaction between the θ-alumina and perovskite enhancing reactivity of the perovskite surface and lattice oxygen.

POM catalyst activity characterized by methane conversion correlates in general with their activity in reforming reactions (Fig.1). This implies that at least a part of methane is converted into syngas via the indirect route involving combustion of methane followed by subsequent reforming reactions of remaining methane molecules.

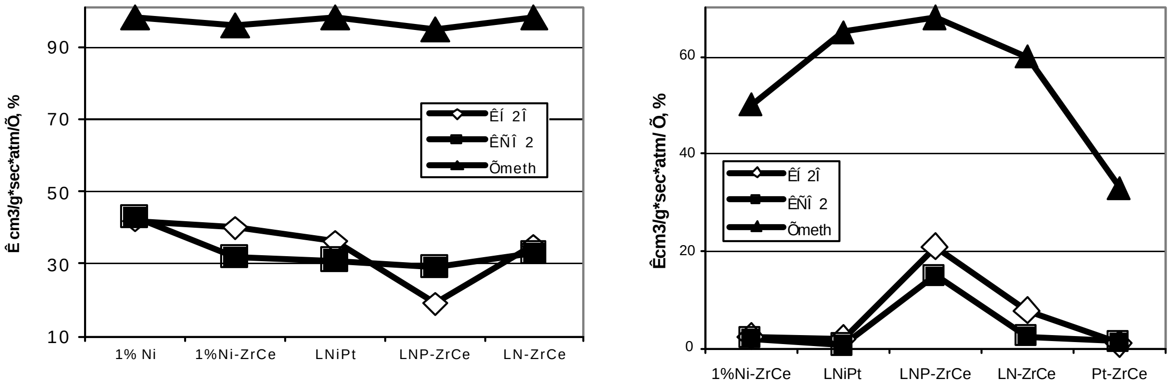

Fig. 1. Steam and dry reforming effective rate constant K and methane conversion in CPO for different active components supported on pure corundum (left) and containing θ-Al_2O_3 (right). L=La, N=Ni, P=Pt.

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CATALYSTS BASED ON SILVER AND COPPER FOAMS FOR ALCOHOL PARTIAL OXIDATION

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High-porous cellular materials (foam metals) represent a very promising type of structural materials for some fields of science and technology including catalysis. Foam metals have uniform cellular structure with anisotropy of mechanical and gas-dynamic properties. Geometrical parameters of the elementary cell are set by the preparation conditions and can be varied within 0.5-5.0 mm diameter. Properties of the whole block change depending on the cell average diameter: porosity (hollow volume) - 80-98 %, volume density (specific weight of the foam-metal block) – 0.1-0.5 g/cm^3. The foam catalyst strength depends on the sample porosity that is explained by changing the density and gauge of lintels between nodes of the cells. Foam catalysts have a high gas permeability close to that of honeycomb samples but far beyond the value for granular ones.

The bulk and supported foam-silver, foam-copper and Ag-Cu catalysts were tested in oxidation of methanol to formaldehyde, ethanol to acetaldehyde and ethylene glycol to glyoxal under different operating conditions. For comparison, specimens of commercial crystalline catalysts and 40 % Ag/pumice and Cu/pumice were tested under the same conditions.

A high porosity of foam materials results in their satisfactory gas permeability. Gas-dynamic measurements showed that the specific pressure drops in filtration of gases through the foam catalysts are considerably lower than the parameters of the granulated and crystallized catalysts.

Experiments showed that the bulk foam-silver and supported on foam ceramics catalysts maight operate efficiently under "soft" (500-550°C) and "hard" (600-700°C) conditions. In the "hard" mode the selectivity of foam-silver greatly exceeds that of the supported catalysts. This is associated with the fact that the foam-silver catalyst contains no support or other inert additives whose surface would be characterized by the occurrence of processes of deep oxidation and carbon deposition. It is well known that coking is the main reason for deactivation of the supported silver catalysts after operation for 3-6 months. Therefore, the foam-silver catalyst may be used over a period 2-3 times longer than the supported one. This greatly reduces the additional cost of increasing (by approximately a factor of 1.5) the specific load of silver in the reactor.

The catalytic characteristics of the foam catalyst and crystalline silver in "soft" mode are comparable. However, gas permeability of the foam catalyst is considerably higher than that of the crystalline one. Silver crystals during the high-temperature reaction are gradually sintered, form a compact mass and inhibit the passage of the gas flow. Sintering of silver is the main reason for gradual deactivation of the crystallized catalysts after operation for 1-1.5 years. Under the "hard" conditions sintering takes place at a considerably higher rate - over several months. The foam-silver catalyst has a three-dimensional cellular structure where the individual parts of the active surface are not in contact with each other and are not therefore sintered. Electron micrographs show that under the effect of the reaction medium development of the surface of the foam catalyst is caused by partial microcrystallisation of the surface layer of the metal. The low volume density of the foam catalyst enables the specific load of the precious metal to the reactor to be reduce by a factor of 1.5-2 times in comparison with crystalline silver.

The foam-copper and Cu-Ag catalysts and, for comparison, crystallized copper and Cu/pumice samples were tested in the processes of selective oxidation of methanol and ethanol under the same conditions. The experiments revealed that selectivity of the foam-copper catalyst exceeds the one of Cu/pumice and $Cu_{cryst.}$ specimens but is lower than selectivity of the foam-silver catalyst. Tests of the foam-copper catalyst with the supported silver layer showed that at the beginning of the experiment this sample had catalytic properties close to that of the foam-silver catalyst. However, after 4-6 hour of work selectivity of the sample decreased significantly. Micrographs showed that in the exhausted catalyst thin silver layer is destroyed, silver partially dissolved in copper or aggregated in small "droplets" on the surface of the foam metal. So, Cu and Cu-Ag foam catalysts are not effective in the studied processes.

Activity of the foam catalysts depends strongly on the cell size. Fine-cellular samples (0.8-1.0 mm) have better selectivity in aldehyde synthesis as in the hollow volume of big cells the processes of deep oxidation and destruction of the products occur.

Different electronic states (ions, charged cluster, crystals) of silver and copper on the catalyst surface were studied by method of electron spectroscopy of diffuse reflectance. On the base of catalytic and spectroscopic data we made a conclusion on the nature of the catalyst active sites.

CELLULOSE PYROLYTIC DEGRADATION IN THE PRESENCE OF SOME AMMONIUM METALATES

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Cellulosic materials are widely used as carbon precursors in preparation of carbon adsorbents and catalysts [1,2]. Because of a great variety of side reactions accompanying the pyrolytic degradation of cellulose (depolymerization, cracking, etc.), the carbonization of cellulosic materials is associated with considerable losses in carbon and is characterized by relatively low char yields [2]. To increase the selectivity of the above process for carbon, cellulose pyrolysis is often conducted in the presence of various catalytic additives [2].

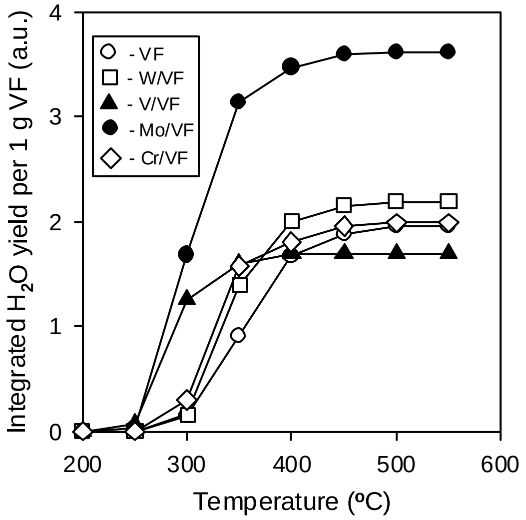

Fig. 1. Influence of ammonium metalates on the temperature dependences of integrated H_2O yields during the pyrolytic degradation of viscose fibers (amount of the additive in all modified samples – 3.64×10^{-4} M Me/1 g VF).

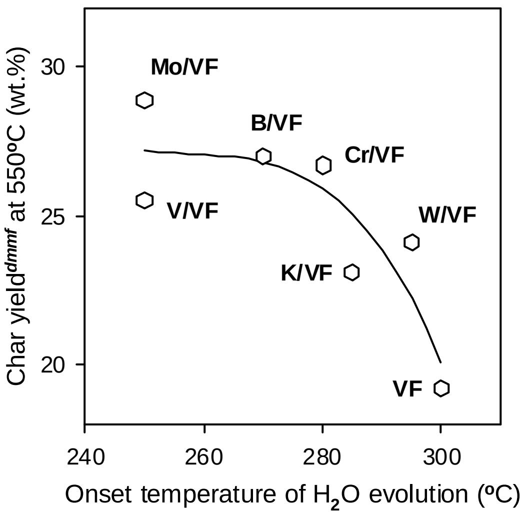

Fig. 2. The relationship between char yields (at 550°C) and onset temperatures of H_2O evolution during the pyrolysis of modified VF-based cellulosic materials.

In the present work catalytic effects of $(NH_4)_2Mo_2O_7$, NH_4VO_3, $(NH_4)_{10}W_{12})_{41}\cdot 5H_2O$, and $(NH_4)_2Cr_2O_7$ on char yields and evolution of gaseous products (H_2O, CO_x) during temperature-programmed pyrolysis (10°C/min, 20-550°C, 25 ml He/min) of viscose fibers (VF) have been investigated. The experimental details are described elsewhere [3]. For comparison, similar pyrolytic experiments were performed for KOH- and H_3BO_3-modified VFs. The results obtained indicate the increased char yields (relative to additive-free cellulosic samples during the pyrolysis of VFs in the presence of inorganic additives, with charring efficiencies (char yields calculated on a dry mineral matter-free base) decreasing in the order of: Mo (28.9%) > B

(27.0%) ~ Cr (26.7%) > V (25.5%) > W (24.1%) > K (23.1%) > without additive (19.2%). It has been established that a definite relationship exists between processes of H_2O evolution in the course of cellulose pyrolysis and char yields obtained. Thus, with increasing H_2O yields at early stages of cellulose decomposition (T < 350°C) and with decreasing the onset temperatures of water evolution, char yields tend to rise (cf. Figs. 1-2). Based on the correlations between electronegativities (EN) of the additive cations, their dehydration and charring effects (Figs. 1-3), catalytic activity of ammonium metalates were associated with their acidic properties that facilitate the processes of cellulose dehydration and subsequent condensation of intermediates formed at early stages of cellulose pyrolysis. We have no a quite plausible explanation for the relatively weak effect of W (VI) species on VF carbonization (see Fig. 3). Possibly, onset temperature of H_2O evolution and amounts of water released at low temperatures are more important parameters for cellulose carbonization than the total H_2O yield during cellulose pyrolysis. Such an assumption is, to some extent, supported by the results presented in Fig. 4. Char yields obtained at 550°C (at the end of the experiment) are almost directly proportional to H_2O fractions in the gaseous products evolved during earlier stages (up to 350°C) of cellulose pyrolysis.

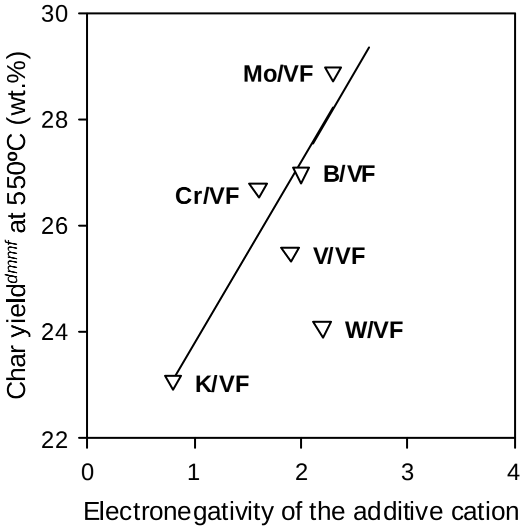

Fig. 3. The relationship between the EN values of the additive cation and char yields (at 550°C) obtained during the pyrolysis of modified VF-based cellulosic materials.

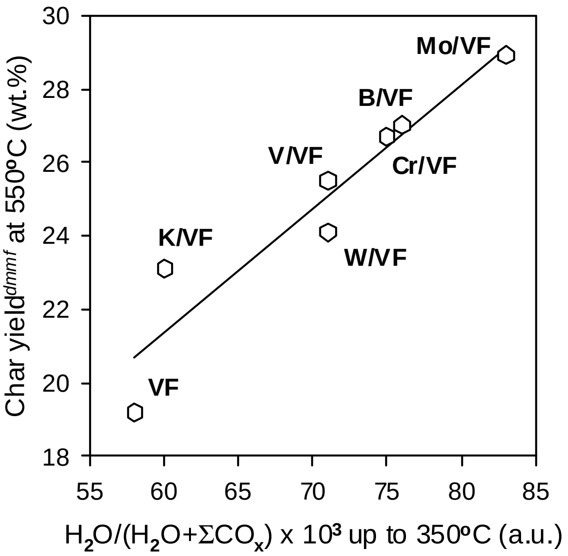

Fig. 4. The relationship between char yields at 550°C and H_2O fractions in the gaseous products evolved during the pyrolysis of modified VF-based cellulosic materials up to 350°C.

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CATALYSIS IN ENERGY SAVING TECHNOLOGIES FOR FUEL PRODUCTION FROM BIOGENIC RAW MATERIAL AND ORGANIC WASTES

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Development of the technologies for organic wastes utilization and processing of natural resources with the aim of energy production is of great importance from the viewpoints of energy saving and ecology. The use of catalysis allows increasing the processes efficiency and solving a number of technological problems via reducing of production expenses, simplification of apparatus system, increasing of organogenic substances conversion, and increasing of ecological safety. Such technologies are used for the processing of renewable (biomass and organic wastes) and partially renewable (peat) energy resources.

Main ways for energy production from natural resources and solid organic wastes include combustion, gasification, and pyrolysis [1]. Combustion proceeds with high heat allocation, but in the most cases the products contain toxic substances polluting the environment (oxides of sulfur and nitrogen, dioxins, furan, polyaromatic hydrocarbons, arsenic, chromium, cadmium).

Modern technologies of thermal utilization may be divided according to the following characteristics [2]: heating rate (fast and slow pyrolysis); pyrolysis medium (vacuum, hydropyrolysis, methanopyrolysis). Conventionally, in industry the pyrofuel yield from the solid raw material is about 74 wt.%. Industrial annual output is 300,000 tons of pyrofuel, which is used as a substrate for chemical syntheses and a fuel for boiler-houses and electricity production [3].

The process of low-temperature catalytic pyrolysis of the secondary resin articles (tire-covers) allows obtaining mixture of combustible gases, which can be used as an energy source for central heating and hot-water supply. At 400°C the yield of gases is rather high in comparison with that in the temperature range of 320-360°C. The mixture obtained at 400°C is characterized by lower combustion heat in comparison with the mixture obtained at 460°C, but in the former case the highest yield of hydrocarbon is observed and a lower amount of solid rest is formed. Chlorides of VIII group metals (Fe^{+2}, Co^{+2}, Ni^{+2}) with the metal content of 0.1, 0.25, 0.5, 1.0, 2.0, 3.0 wt.% of substrate loading were studied as catalysts. Maximum combustion heat was found for the mixture containing 1% of Ni-catalyst. This can be explained by maximum yield of propane, which is characterized by the highest combustion heat among the other obtained gases.

To provide analytical control over pyrolysis, a complex of laboratory units was elaborated, which included analyzer of the lowest volumetric specific heat of combustion, analyzer of volumetric concentration of hydrogen in gas, and chromatographic analyzer of gaseous hydrocarbons in gas media.

Apart from utilization of solid wastes, there is a problem of maximum full usage of natural resources. As it is known, industrial plants on chemical processing of organic fuels pollute environment to a great extent, hence, radical improvement of existing technologies is of urgent interest.

Application of catalytic pyrolysis in the processing of biogenic fuel (peat) allows obtaining combustible gas (with high combustion heat) at lower temperatures than in non-catalytic process that solves ecological and technological problems without the reduction of heat-generators efficiency. The pyrolysis experiments were conducted at 400°C with $NiCl_2$ and Lewis acids as catalysts ($AlCl_3$, $ZnCl_2$) in the range of metal concentration of 0.25-5 wt.%. Alumosilicate materials (clay) were used as well in the amount of 30%. The use of 1% $AlCl_3$ leads to the decrease of activation energy to 10 kJ/mol and the increase both of thermodestruction rate and yield of combustible gases. The use of alumosilicate materials leads to the 2-fold increase of combustible hydrocarbons yield.

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STUDY ON BIODESTRUCTION OF THE WOOD WASTES LIGNIN AS AN INITIAL STAGE OF THE HUMUS-LIKE SUBSTANCES PRODUCTION

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Introduction

The main reason of a lot of modern ecological problems is a local accumulation of organic wastes in the quantities exceeding the natural biodegradation potential. The problem could be solved via biodestruction of organic wastes (woodworking industry wastes), as this process allows obtaining valuable product along with purification. Wastes' treatment with microorganisms or enzymes leads to stable products of biological oxidation. Humus achieves equilibrium with ecosystem rapidly and does not lead to serious damage as untreated wastes do.

Some representatives of Basidiomycetes and Proactinomyces are known to accumulate humus-like substances in large quantities. That is why the study of biosynthetic pathways of humus-like substances produced by lignin-degrading microorganisms is of current interest. The most important hypotheses of humus formation are based on the idea of humus acid formation via partial transformation of natural biomolecules or the interaction of structural units by means of enzyme complex (phenol oxidase, laccase, cellulase, etc.)

Materials and methods

The culture development of Proactinomyces of Nocardia genus was sustained in agar-based medium of Chapek-Docks in retorts at steady conditions of 25°C for 30 days. 10 g of the crushed substrate (sawdust) and 50 mL of the medium without glucose were put to each retort. 30 mL of inoculate were added after sterilization. The samples of sawdust obtained after bioconversion were studied in terms of ashes content, residual mass, celluloselytic and ligninolytic activities, content of hardly hydrolyzed polysaccharides. Lignin extraction was performed by the modified method of Komarov. IR-spectra of the obtained substances were recorded with FT-IR-spectrometer FT-10 (S.-Petersburg).

Results and discussion

Proactinomyces were found to use first cellulose and then lignin as a substrate during cultivation. Peripheral cellulose is proposed to be decomposed first as it is accessible for microbiological cellulases. Lignin molecules hamper cellulase access to the residual cellulose that makes difficult further cellulose hydrolysis.

Along with lignin concentration decrease in the substrate, slow increase of humus-like substances was observed.

IR-spectra of the extracted sulfolignins coincide with literature data. They were identified by the presence of characteristic bands in the range of 1590 cm^{-1} (aromatic ring), 1130 cm^{-1} (methoxylic groups), 2800-3000 cm^{-1} (methyl and methylene groups). After the fermentation, the peaks were detected in the range of 667 cm^{-1}, which can be attributed to the sulfa-groups of sulfolignin. Besides, the absorption intensity in the range of 2800-3000 cm^{-1} decreased indicating the decrease of the amount of methyl and methylene groups of the obtained sulfolignin. The absorption intensity in the range of 1596-1485 cm^{-1} changed as well.

Thus, on the basis of literature data [1,2] and experimental results, one can propose that the change in lignin structure proceeds via enzymatic demethoxylation, while the humus-like substances being formed via lignin destruction and following synthesis with biomolecules of microorganisms.

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OXIDATIVE BROMINATION OF AROMATIC COMPOUNDS

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The halogenation is one of the most well studied and widely applied reactions of the compounds of aromatic series. However, in the industry the chlorination is used only on a large scale, the bromination is applied much less, and iodination is applied only in a few cases. It is explained by higher cost of bromine and iodine in comparison with chlorine, and also by decrease of reactivity in the row Cl > Br > I. With the purpose of more complete using of halogens and increasing of their reactivity the halogenation frequently is carried out in the presence of strong oxidants: HNO_3, $Na_2S_2O_8$, HIO_3, NaClO. We have shown that the catalytic additives of nitrogen oxides ($NaNO_2$, HNO_3) allowed to utilize the oxygen as an oxidant and to carry out the bromination of arenes with high activity.

In the system H_2SO_4 - $HNO_3(NaNO_2)$ - H_2O - O_2 the oxidative bromination of arenes submits to the stoichiometry of reaction:

$$ArH + HBr + ?\ O_2 \xleftrightarrow{k} ArBr + H_2O \qquad (1)$$

The process of oxidative bromination of arenes in the presence of hydrogen nitrate begins by emitting of small volume of gas (10-30 ml at 323K), then during some time the volume of gas does not change, potential of the system grows on 0,2-0,4 V. To our opinion at this time there is forming the active form of catalyst - NO_2

$$6HBr + 2HNO_3 \xleftrightarrow{k} 3Br_2 + 2NO + 4H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

The redox potential of the system is described by the equation:

$$j = 1{,}09 + \frac{RT}{F}\ln\frac{[NO_2]\cdot g[H^+]}{[HNO_2]} = 1{,}065 + \frac{RT}{F}\ln\frac{[Br_2]}{[Br^-]^2}$$

The intensive oxygen absorption begins at the accumulation of the certain amount of NO_2 (φ=0,8 - 1.0V). During the reaction (1), the potentials of investigated systems practically do not change. After absorption of stoichiometric quantity of oxygen ($Q_{O_2} = 1/2C_{ArH}$) potentials of the solution grows on 20 – 30 mV, and the rate of reaction (1) decreases to 0. IR-spectra behave similarly, demonstrating that the quantity of formed NO_2 increases in the beginning of experiment and at the end of reaction remains constant during bromination of ArH.

The reaction product represents light yellow water-insoluble fluid, in the case of using of o-xylene the product has density of 1,35 g/cm^3, boils with decomposing in temperature range 175-185°C at 694 mm, and is characterized by negative reacting with alcohol solution $AgNO_3$ and NaI. According to PMR and NMR ^{13}C data the admixture is richest by 4-Br-o-xylene.

The obtained experimental results are described by the kinetic equation:

$$\frac{-a\text{Ñ}_{ArH}}{at} = \frac{k_j \cdot \sum_{j=1}^{2} g_j \cdot a^{j}_{H_3O^+} \cdot C_{ArH} \cdot a_i \cdot C_I}{\sum_{j=0}^{2} g_j \cdot a^{j}_{H_3O^+} \cdot \sum_{i=0}^{1} C_{ArH} \cdot a}$$

Here γ_j α_i is constants of protonisation of NO_2 and complex formation of ArH with Br_2 correspondingly.

For o-xylene at T=323K $k_1=2,5\cdot10^{-3}$ s^{-1}, $k_2=1,3\cdot10^{-2}$ s^{-1}, $\gamma_1=$ $5,7\cdot10^{-4}$, $\gamma=$ $7,8\cdot10^{-4}$, $\alpha=0,9$ l/mol.

For investigated arenes: nitrobenzene, n-nitrotoluene, benzene, toluene, o-xylene, m-xylene, n-xylene, mesitylene, durene, the dependence of the first order rate constant from a nature of the arene substituents is described by the Gammete equation:

$$\ln k_2 = \ln k_2^o - \rho\cdot\sigma^*$$

were $\ln k_2^o$ = -7,7 and -7,5; ρ = -3,8 and -2,9 at 323K and 338K correspondingly.

Analysis of these magnitudes demonstrates that at T=323K as well as at iodination of arenes, in a limiting stage of bromination of benzene and its homologues the base role is played by a σ-complex, and the activity of bromide σ-complex is higher than iodide one and more strongly dependes on electron-donating capacity of the substituents.

At T≥338K there is a variation of the structure of the transitional state of the reaction (1) ($\alpha\rho/\alpha T>0$), and the most slow stage appeared to be formation of the π-complex. The variation of the structure of the transitional state is confirmed by isomers distribution. If at T ≤ 323K an interrelation formed is ortho- and para-Brom- toluenes 1:4 (σ-complex), at T ≥ 338K the base product is ortho-Brom-toluene.

OXIDATIVE IODINATION OF AROMATIC COMPOUNDS

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Unlike other reactions of halogenation the process of iodination is reversible:

$$ArH + HI + 1/2O_2 \leftrightarrow ArI + HI \qquad (1)$$

Therefore it proceeds in the presence of the compounds containing iodide-ions in strong complexes, or in the presence of oxidants. The activity of molecular iodine in reaction (1) is so low, that benzene and its homologues without catalysts does not produce appreciable amounts of iodinated products.

We have shown that in solution H_2SO_4 - NOx - $Co(NO_3)_2$ - KI - H_2O in the presence of oxygen at 35-36°C quantitative oxidative replacement of hydrogen atom of the benzene ring by iodine proceeds according to the stoichiometric equation:

$$ArH + HI + 1/2O_2 \rightarrow ArI + H_2O \qquad (2)$$

The extent of iodine consumption in optimal conditions reaches 99,8%. In the case of using of o-xylene the stoichiometric amounts of yellow oily product having density 1,63 g/cm^3 and boiling point 188°C at 700 mm is formed. The alcohol solution of $AgNO_3$ does not yield sediment even at boiling with the formed product, that points to the ring halogenation. According to the data of PMR and NMR ^{13}C the obtained product is 4-I-1,2-dimethylbenzene.

Kinetic, potentiometric and spectrophotometry investigations have shown, that in the absence of $Co(NO_3)_2$ oxidative iodination of ArH in the system $NaNO_2$ - $HClO_4$ - KI - H_2O - proceeds through series of the base reaction:

$$2HNO_2 + 1/2O_2 \rightarrow 2NO_2 + H_2O \qquad (3)$$

$$HI + NO_2 \rightarrow 1/2I_2 + HNO_2 \qquad (4)$$

The IR-spectra of a gas phase and solution have shown, that the quantity of formed NO_2 increases at the beginning of the process as a result of reaction (3), and at the end of reaction, when $C_{ArH} > 0$, remains constant during ArH iodination. The given fact testifies to a catalytic role of NO_2 in common process. The detailed study of kinetics of reaction (1) has shown, that the catalytic activity of NO_2 increases as the acidity of solution increases.

The dependence of rate of iodination of arene on $a_{H_3O^+}$ is described by the equation:

$$W\frac{k_1\cdot g_1\cdot a_{H_3O^+}+k_2\cdot g_1\cdot g_2\cdot a^2_{H_3O^+}}{1+g_1\cdot a_{H_3O^+}+g_1\cdot g_2\cdot a^2_{H_3O^+}}, \qquad (5)$$

were γ_1 and γ_2 is constants of equations:

$$NO_2 + H^+ \xleftrightarrow{g_1} NO_2H^+;\ NO_2H^+ + H^+ \xleftrightarrow{g_2} NO_2H_2^{2+}$$

Kinetic and thermodynamic constants of the equation (5) are summarized below:

T, K	k, c^{-1}	γ
323	$k_1 = 0{,}03$	$1{,}4\cdot10^{-3}$
	$K_2 = 0{,}28$	$1{,}3\cdot10^{-5}$

The effect of the nature of the substituents in the benzene ring on kinetics of iodination is described by the Gammete equation:

$$\ln k_2 = \ln k_2^{o} + \rho\cdot\sigma^+$$

were $\ln k_2^{o}$ = -8,75 and -7,2; ρ = -1,7 and -2,1 at 323K and 338K accordingly.

The linear correlation of $\ln k_2$ on σ^+ points, that the reactive center is in the aromatic ring. A negative value ρ testifies electrofilic nature of a limiting stage. The negative temperature dependence of ρ points that variations of structure of a transitional state does not occure ($\Delta\Delta S^{\neq}=0$).

For finding out the most probable electron and geometrical structure of the active oxidative forms of NOx we have used CNDO quantum-chemical method.

THE CATALYTIC CONVERSION OF CARBOHYDRATES INTO THE LEVULINIC ACID AND 5-HYDROXYMETYLFURFURAL DERIVATIVES

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Hexose carbohydrates, like cellulose, sucrose and fructose are known to produce levulinic acid (LA) and 5-hydroxymetylfurfural (HMF) in the acid media under rigorous conditions (above 160°C). Levulinic acid is applied for the polymer production and in other different fields of chemical industry and researches. LA is also formed at moderate temperatures about 100°C and high acidity of the solutions, but such processes have not been comprehensively studied. The low yield of the products is the great problem of the processes, and the main aim of this work is to increase the selectivity of the acid-catalyzed conversion of carbohydrates applying the alcohols as extractants of the products. The rate of LA formation from glucose slightly depends on HCl concentration but selectivity of the process strongly increases with raising H_0 (Fig. 1). Such selectivity gain can be explained by raising the water activity and decreasing the contribution of pathways connected with the reactant and intermediate condensation into humic substances. Indeed, the water activity estimated as the ratio of vapor pressure of the solution and pure water, is approximately proportional to H_0 in the conditions discussed. Hydrochloric acid is twelve times more active than sulfuric acid, but selectivities of the LA formation are practically the same in both cases (35 – 38 mol. %). Phosphoric acid is too weak for application as the catalyst of the process: the maximum yield of levulinic acid does not exceed 5 mol. %, and the rate of process is small (Fig. 2). To explain these ratios of the rates and yields one may take into account the known approximate connection between H_0 and activities of H_2O and H_3O^+: $H_0 = a - \lg (X(H_3O^+)/X(H_2O))$ (1) According to the equation (1) the necessary H_0 value can be attained either by increasing $X(H_3O^+)$ for the strong acids or by decreasing $X(H_2O)$, the water activity in the case of weak acids. The comparison of the results performed in Fig. 1 and 2 shows that the water activity, but not Hammett acidity function, is responsible for the selectivity of the levulinic acid formation. Sulfuric acid like hydrochloric permits to attain good selectivity of producing levulinic acid. Butanol is the efficient and available extractant for levulinic acid (the distribution coefficient k = 4). It forms the stable two-phase system with water, but concentrated sulfuric (above 5,1 M) and hydrochloric acids are known to give homogeneous solutions with the alcohol. To prevent homogenization we apply the mixture of sodium sulfate and sulfuric acid as the catalyst (sodium bisulfate with or without the addition of sulfuric acid). This approach allows creating the stable two-phase system water – butanol with good catalytic activity. The main products of the acid-catalyzed sucrose conversion in the presence of butanol are butyl levulinate and 5-butoxymethylfurfural. Their structures are confirmed by GC-MS, ^{13}C and ^{1}H NMR spectra. Under optimum conditions (4.6 M $NaHSO_4$) the total yield of the products attains 60 mol. % from sucrose and 83 mol. % from fructose. The method developed is much more efficient than the known synthesis from chloromethylfurfural. To increase the selectivity of the process by extracting the products from the reaction mass the flow unit was constructed and the process of the carbohydrate acid conversion in the flow of butanol was studied. The main problem of such process is the extraction of fructose or intermediate of its conversion, and these effects do not permit to attain good yields of the products.

ALKYLATION OF BENZENE WITH PROPENE ON BETA ZEOLITES UNDER SUPERCRITICAL CONDITIONS

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Cumene is an important intermediate product due to its elegant conversion into phenol and acetone. It is manufactured exclusively by the alkylation of benzene with propene in gas (G), vapor (V) or liquid (L) phase and an excess of benzene is normally used to minimize the facile further alkylation of cumene [1]. Recent process developments concern the use of zeolites as catalysts, which could be an alternative for a more environmentally friendly and noncorrosive process without the release of acidic catalyst components [2]. However, the catalyst deactivation due to the carbonaceous deposition at a high proportion of propene and high space velocity is still an essential problem.

Performing heterogeneously catalyzed reactions in a supercritical fluid (SCF) rather than in a G, V or L phase could be an interesting option for increasing throughput and prolonging catalyst lifetime [3,4]. In our previous work, the alkylation with a benzene/propene mole ratio of 5 on a series of β-zeolites in different phases was inspected [5]. The highest yield of cumene and stability of the catalysts were observed when the reaction was carried out under supercritical conditions near the critical point. However, the different phases were categorized according to the V-L equilibria of the binary system of benzene + propene, which is actually improper because the composition and related critical properties of the reacting mixture change always along the reaction course.

To capitalize on the unique characteristics of the reacting medium under supercritical conditions, it is essential to be cognizant of the critical properties of the reacting mixture along with the reaction course [6]. Therefore, the critical properties of both binary and ternary mixtures involved in the alkylation of benzene with propene were measured by using a high-pressure view cell with visual observation in this work. Moreover, the critical properties of the ternary mixture were determined with the compositions representing the extent of alkylation. As shown in Figs. 1 and 2, the critical properties of the reacting mixture change upon the reaction proceeding at a certain initial ratio of benzene to propene; as the reaction proceeds to a higher propene conversion, the critical temperature shifts to a higher value while

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the critical pressure to a lower one. Therefore, to ensure that the reaction was carried out under supercritical conditions near the critical point, the reaction conditions should be tuned up according to the critical properties of the reacting media along the reaction course.

To compare the reaction behaviours in different phases, the catalytic tests were carried out over Hβ at pressures and temperatures which covered all these regions shown in Fig. 1 (initial mole ratio of benzene/propene = 4, benzene LHSV = 59.6 h^{-1}). As shown in Figs. 3 and 4, the reactions under different situations were quite different in the behaviours. The selectivity to cumene was about 90% in all the tests since a high space velocity was used. The catalysts deactivated much more rapidly when the reactions were carried out under such conditions far from the critical region of the reacting mixture, while they showed much longer lifetimes under the conditions near the critical region of the reacting mixture (290–310 ^{o}C, about 5.7 MPa). Especially, the catalyst lifetime reached 230 h when the reaction was carried out at 300 ^{o}C and 5.7 MPa; during the reaction, this point should belong to a region of SCF to L near the critical points of the reacting mixture.

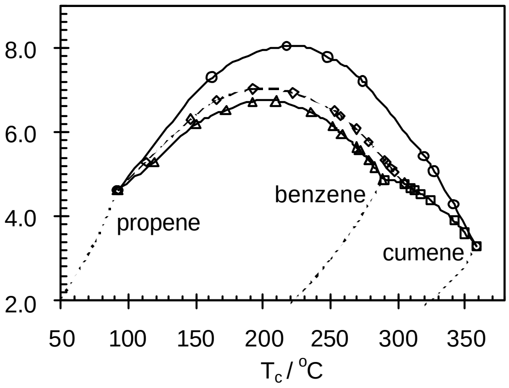

Fig. 1. Critical point loci of the binary and ternary mixtures in P-T projection (dotted lines, the vapor pressure of pure component)

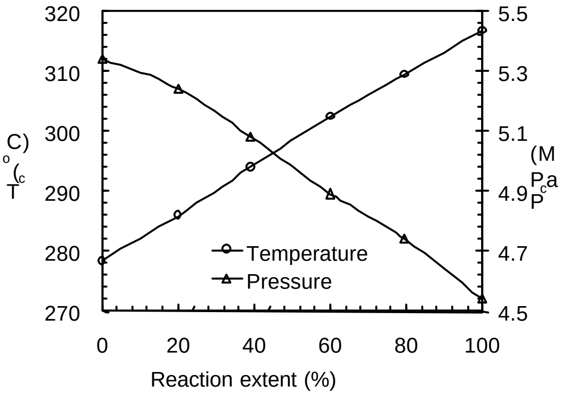

Fig. 2. Critical temperature and pressure of reactants mixture along the reaction course with the initial mole ratio of benzene/propene being 4.

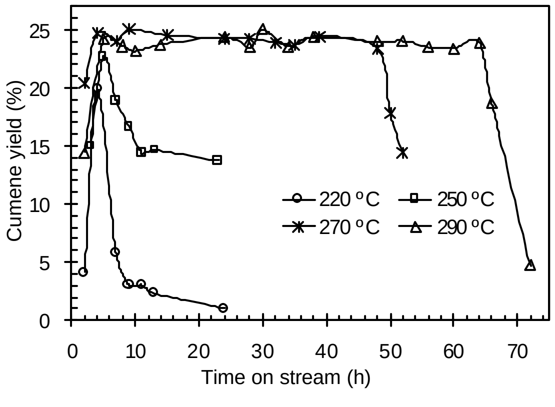

Fig. 3. Cumene yields at near critical pressure (6.5 MPa) under different temperatures.

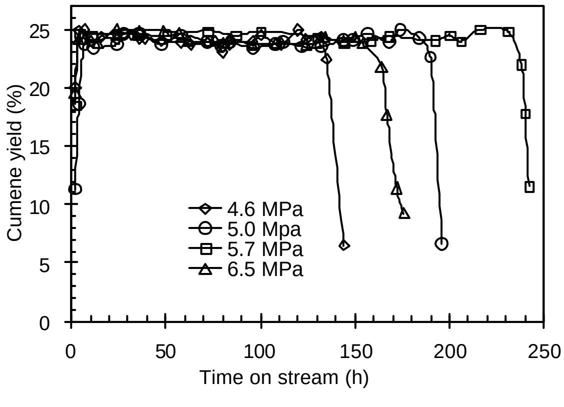

Fig. 4. Cumene yields at near critical temperature (300 °C) under different pressures.

In conclusion, the alkylation of benzene with propene over Hβ zeolites under different reaction conditions proved that the supercritical reacting media was efficient to improve the reactivity, to prolong the catalyst life, and hence to boost the production capability significantly. However, the reaction conditions should be determined according to the critical properties of the reacting mixture along the reaction course.

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MUTUAL INFLUENCE OF CO AND H_2 DURING THEIR OXIDATION ON $CuO/Ce_{0.7}Zr_{0.3}O_2$ CATALYSTS

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The development of effective catalysts for oxidative removing of CO impurities from hydrogen-enriched mixtures is an actual problem [1-3] which is connected with the perspective of H_2 using as an energy carrier. The presence of carbon monoxide in H_2 is unacceptable because of its poison action on Pt-electrodes of fuel cells.

Noble metals and copper based catalysts [4-9] were proposed for selective oxidation of CO in H_2 enriched mixtures. The mutual influence of CO and H_2 during their oxidation was observed in several investigations [4, 6, 7]. However, this effect substantially changes depending on the type of catalysts and process conditions. In this connection it is of interest to study this problem for CO oxidation on the high-performance Cu-Ce-Zr-O systems [8, 9].

The catalysts were prepared from nitrates of Cu^{2+}, Ce^{3+} and ZrO^{2+} by decomposition of their mixtures in air at 300 °C for 2 hours. Catalytic tests were carried out in flow microreactor (quartz tube, internal diameter of 6 mm) at atmospheric pressure with catalyst powder (0.05 g). The gas mixture compositions (vol. %): $2\%CO+1\%O_2+4\%N_2+46\%H_2+47\%He$ (mixture 1); $2\%CO+1\%O_2+4\%N_2+93\%He$ (mixture 2); $1\%O_2+4\%N_2+46\%H_2+49\%He$ (mixture 3). The GHSV was 35000 h^{-1}. The reaction rate constants were calculated from the values of CO, O_2 and H_2 conversions according to integral kinetic equations [9].

The rate constants of CO and H_2 separate oxidation (mixtures 2 and 3) are higher then that for mixture 1 which contains both oxidizing components (Table). It follows that CO hinders H_2 oxidation and hydrogen retards the oxidation of CO. The activation energies of CO and hydrogen oxidation are practically the same for all reaction mixtures. Therefore it is possible to conclude that the increasing of rate constants under CO and H_2 separate oxidation is connected with the increasing of preexponential factors. It indicates that quantity of active centers taking part in the reactions changes as a result of the competitive adsorption of CO and H_2.

Table.

The constant rates (mole×$g_{cat.}^{-1}$×h^{-1}×·atm^{-2}) and Arrenius parameters (E, $\ln k_0$) of CO (k_1) and H_2 (k_2) oxidation for various gas mixtures on 5%CuO/$Ce_{0.7}Zr_{0.3}O_2$.

T, °C	Combined oxidation (mixture 1)		Separate oxidation	
	CO	H_2	CO (mixture 2)	H_2 (mixture 3)
	k_1	k_2	k_1	k_2
60	0.0690	0.0011	0.0808	-
80	0.196	0.0038	0.481	0.0426
100	0.661	0.0169	1.95	0.0591
120	3.01	0.0428	12.7	0.198
140	16.2	0.195	-	0.693
160	-	-	-	2.78
180	-	-	-	13.3
E, kcal/mol	18.4 ± 1.7	17.3 ± 0.9	21.4 ± 1.2	18.5 ± 2.2
$\ln k_o$	24.9 ± 2.3	19.4 ± 1.2	29.9 ± 1.7	22.7 ± 2.8

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NEW SYNTHETIC WAY TO $CuO+ZrO_2$ CATALYSTS AND THEIR INVESTIGATION BY EPR AND ESDR

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Samples of ZrO_2 and $CuO+ZrO_2$ (0.5-100 at. % Cu) were synthesized from $Cu(NO_3)_2{\cdot}3H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$ in molten NH_4NO_3 $\{\nu(NH_4)=(\nu(Cu)+\nu(Zr))\nu 5\}$. After decomposition of mixture, products were annealed in furnace at 500–700 °C during 2 h. Electron microscopy and porosity measurements showed that the samples obtained consist of mesoporous particles with dimensions 10-100 μm.

The lines of t- and m-ZrO_2 present in the XRD-pattern of pure ZrO_2 phase. The XRD-patterns of Cu-ZrO_2 up to 20 at. % Cu show only the lines of c-(t-)ZrO_2 and do not contain the lines of CuO. Metastable t- and c-ZrO_2 phases transform to stable m-ZrO_2 by annealing at T > 600 °C. This is accompanied by formation of crystal CuO and decrease of specific surface area. The last should be caused by segregation of CuO in pores as a result of system CuO-c-(t-)ZrO_2 degradation. Maximum solubility of CuO in ZrO_2 according to XRD is 20-25 mol. %. It is confirmed by results of X-ray spectra element analysis.

The information obtained from electron spectra for Cu-ZrO_2 in diffusion reflection (ESDR) is following:

1. There is an edge of the fundamental adsorption (EFA) for ZrO_2 ~ 37000-40000 cm^{-1}. It does not depend on annealing temperature and copper content in the sample. The edge of the fundamental adsorption is overlapped by extra adsorption of copper oxide clusters at 27000 – 32000 cm^{-1}. It can be noted that at low copper content (0.5 at. %) energy of these bands is close to energies of bands of charge transfer of copper oxide cluster found previously in different copper catalysts.
2. There are d-d-transitions of isolated ions Cu^{2+} ions at 13000 – 16000 cm^{-1}. Their intensity increases with increase of copper content. Energies of d-d-transitions in ESDR spectra of samples annealed at 500 °C are typical for ions Cu^{2+} in oxygen octahedral crystal fields with tetrahedral distortion (13000 – 14000 cm^{-1}). At the same

time there are very narrow bands in the region 16000 cm^{-1} in spectra of samples annealed at 600 °C and 700 °C. This displacement of d-d-transitions could be explained by distortion of copper octahedral coordination by cooperative effect of Jahn-Teller (CEJT).

3. At high copper content (>30%) ESDR spectra typical to CuO are observed (broad absorption at region 12000 – 20000 cm^{-1} and large general absorption at UV-region).
4. Intensity of the band at 32000-35000 cm^{-1} increase with the increase of copper content up to 1.5 at. % and then does not change. It can be supposed that formation of thin layer of CuO is the reason of the appearance of this band. This is in accordance with that copper content in surface layer is 10-30 % more than average copper content in samples (obtained from data of X-ray spectra element analysis).

Analysis of electron paramagnetic resonance (EPR) spectra show that cations Cu^{2+} in Cu-ZrO_2 samples exist at least in two different forms. EPR spectra of isolated ions Cu^{2+} with $g_{||}$ = 2.36, $A_{||}$ = 126 Gs corresponding to octahedron with tetragonal distortion are observed for samples Cu-ZrO_2 with 0.5 - 3 at. % Cu annealed at 500 °C. In the region $g_{\perp}$ spectra are very complex, but spectrum of exchangeable ions without hyperfine structure is observed. This spectrum is well distinguished for samples with 2 – 3 at. % Cu. Value of $g_{||}$ of exchangeable ions is probably less than $g_{\perp}$, moreover $g_{||} > g_e$. According to the literature this exchange spectrum is caused by ordering of ions Cu^{2+} by CEJT that agree with data obtained by ESDR. The most part of copper exists in the form of associated ions already in sample with only 0.05 at. % Cu. The increase of copper content results in increase of quantity of associated ions observed by ESDR. Also it is interesting that for samples ZrO_2 annealed at 500 °C spectrum EPR of radical NO_2 is observed with rhombic anisotropy of g and A tensors and following parameters: $g_1 = 2.0046$, $g_2 = 2.0015$, $g_3 = 1.99$, $A_1 = 52$ Gs, $A_2 = 67.5$ Gs, $A_3 = 50$ Gs that coincide with well-known data for this radical in absorbed state. Increase of sample annealing temperature to 700 °C leads to disappearance of EPR-spectrum of NO_2-radical and appearance of axial EPR spectrum of ions Zr^{3+} with parameters $g_{\perp} = 1.975$ and $g_{||} = 1.96$. Thus it can be supposed that formation of radical NO_2 and following reduction of ZrO_2 with formation of ions Zr^{3+} (d^1-ion) deals with nitrate synthesis method.

So, it can be said that mesoporous particles of solid solution CuO in c - (t-)ZrO_2 with dimensions 10-100 μm are formed in ammonium nitrate during decomposition. Maximum solubility of CuO in ZrO_2 is 20-25 mol. %. Besides uniform distribution of CuO in ZrO_2 as solid solution CuO forms clusters and thin layer on the surface of solid solution particles.

FUELS AND CHEMICALS FROM BIOMASS

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There are several fermentation technologies to convert biomass to alcohols (ethanol, butanol, isopropanol, etc.). The most common is producing ethanol using yeast. However, alcohol recovery by distillation is energy intensive and in the case of sufficiently dilute fermentation solutions is uneconomical for recovering biofuels (liquid energy carriers). Pervaporation, a membrane separation technique that can separate organics from water, is considered to be one of the best potential separation technologies for recovering alcohols from fermentation broth. Simultaneous removal of the product, on a continuous basis, by applying pervaporation during fermentation eliminates product inhibition, increases productivity and concentrates alcohols selectively (so-called, pervaporative membrane bioreactor). These features make the hybrid process economically feasible, provided that high membrane fluxes and selectivities can be maintained over extended operating periods.

Moreover, a new reaction of reductive dehydration of alcohols (RDA), namely, cyclic and aliphatic alcohols C_2-C_5 was recently found out [RF patent # 2220940, 10.01.2004; RF patent # 2220941, 10.01.2004; M.V.Tsodikov, V.Ya.Kugel, F.A.Yandieva, G.A.Kliger, L.S.Glebov, A.I.Mikaya, V.G.Zaikin, E.V.Slivinskii, N.A.Plate, A.E.Gekhman, I.I.Moiseev, Kinetic and Catalysis, 2004, *in press*]. The reaction yields hydrocarbons with at least doubled hydrocarbon backbones of the initial alcohol. This is a new route to produce hydrocarbons (particularly, high quality fuels and additives) from fermentation-derived alcohols. This paper presents i) results on the development of new high-performance pervaporation materials and membranes, based on poly[1-(trimethysilyl)-1-propyne] (PTMSP), for bioethanol and biobutanol recovery from fermentation broth and ii) the recent data on conversion of alcohols into hydrocarbons by means of RDA.

Three different catalytic systems, $TaCl_5$/n-BuLi, $TaCl_5/Al(i\text{-}Bu)_3$, and $NbCl_5$ were used for synthesis of PTMSP samples. It was found that the catalytic system has a significant influence over the properties of membranes made from PTMSP. Lab-scale techniques for preparing high flux and alcohol selective PTMSP membranes was developed. Most recently, fluxes exceeding 1 kg/m^{2}h at 37^{o}C with butanol/water selectivity of 70 were attained. To our knowledge, this is the highest performing pervaporation membrane yet recorded, with the sole exception of a new composite material developed at TIPS that is based on PTMSP but exhibits a two-fold higher pervaporation selectivity than pure PTMSP [V.V.Volkov, O.I.Buzin, N.V.Ushakov, E.S.Finkelshtein, V.S.Khotimsky, E.G.Litvinova, RF Patent application #2003133700 of 21.11.2003, *unpublished data*]. It was demonstrated that pervaporative removal of ethanol and butanol from bioreactor improved the overall performance of the fermentation process.

Bioalcohols can be further converted into hydrocarbons by means of the new reaction of RDA. In case of ethanol, the content of isoparaffins ranged up to about 90% of total hydrocarbons C_5–C_{10} (Table). A yield of alkanes may run to about 60% at 350^{0}C, 30-50 bar and at alcohol conversion equal to 93%. The rest are oxygen containing gaseous and liquid products of known reactions, namely, condensation of alcohols.

Table. Composition of products for 93% conversion of ethanol in argon atmosphere

Gases		Liquids				Total Yield, %
		Hydrocarbons		Oxygen containing products		
Product	Yield, %	Product	Yield, %	Product	Yield, %	
CO	9.4	n-pentane	2.38	acetaldehyde	0.64	
CO_2	2.64	i-hexanes	36.99	Diethyl ether	9.27	
C_1	2.84	i-heptanes	0.62	butanon-1	0.79	
C_{2-4}	10.44	n-octane	0.31	butanol	1.02	
		i-octanes	7	ethoxybutane	2.74	
		i-octene	0.83	diethoxyethane	0.58	
		n-nonane	0.23	hexanon-1	0.93	
		i-nonane	2.29			
		i-nonene	0.76			
		decanes	1.26			
Subtotal	**25.32**	**Subtotal**	**52.7**	**Subtotal**	**21.98**	**100**

COMPOSITION OF Cu/ZnO AND CuAl/ZnO METHANOL SYNTHESIS CATALYSTS AS PREPARED AND HYDROGEN ACTIVATED BY *IN SITU* XRD AND HR EM

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This study is devoted to the composition of CuZnO catalysts as prepared and after activation with hydrogen. $Cu_{0.08}Zn_{0.92}O$ and $Cu_{0.2}Zn_{0.7}Al_{0.1}O$ were chosen to represent solid solutions of copper and aluminium ions in imperfect zinc oxide. This type of solid solutions, being the precursors of active methanol synthesis catalysts, is formed through decomposition of the respective hydroxocarbonates at 570-770 K [1].

Based on known data and those obtained in this study the following interpretations may be proposed. During the formation of the CuZnO solid solutions, the foreign anions in anion-modified (*am*) oxides give rise to extended stacking faults of (002) ZnO lattice plane (*esf*). These are occupied by copper ions in the form of small clusters of the Cu^{+2}–O–Cu^{+2} type. The nearest oxygen environment of the copper ions in such a cluster is a distorted octahedron, exhibiting a nearly square plane. Aluminium ions dissolved in zinc oxide promote formation of these clusters, and prevent crystallisation of a separate copper oxide phase with increasing copper ion concentration [2].

The main part of copper ions in the Cu^{+2}–O–Cu^{+2} clusters are reduced to Cu^0 in hydrogen at 600 K. This metallic copper diffuses either to the external surface or to vacant inner holes of the *am*-ZnO crystal, and is observed as dark spots at electron micrographs (Fig. 1). At HRTEM micrograph (Fig. 2) it can be seen that these dark spot are made up of Moire fringes parallel to ZnO (002) lattice plane with spacing of about 1 nm. This finding indicates a lattice coherence of the inclusion and the main crystal. Fourier pattern of the image of coherent inclusion (Fig. 3) shows the presence of two crystal lattices: ZnO and Cu^0. Copper atoms in the vacant holes form 2-3 nm clusters of the Cu^0–Cu^0 type. If such a hole is situated in the subsurface layer of ZnO, it seems observable by LEIS as a metallic copper particle covered with ZnO [3].

Copper metal particles on the surface of *am*-ZnO are reoxidized to Cu^{+2} at 600 K in a helium flow containing 0.05 vol. % oxygen (Fig. 4), and according to EM data they come back to the *esf*. The Cu^0–Cu^0 clusters in the holes of *am*-ZnO are not reoxidized under these conditions. The same reduction-reoxidation processes were found to take place in the CuAl/ZnO catalyst.

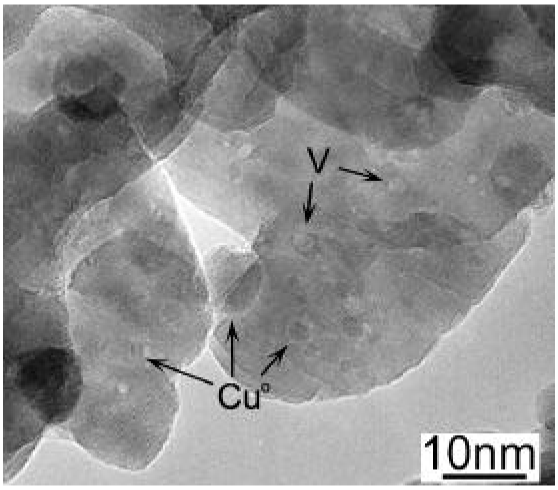

Fig. 1. Electron microscopy image of the $Cu_{0.08}Zn_{0.92}O$ sample reduced in H_2.

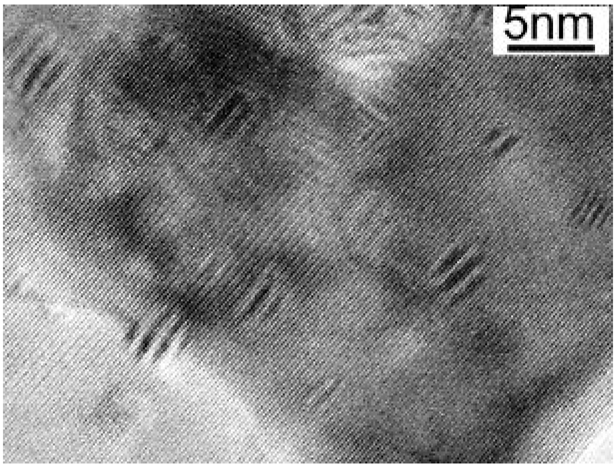

Fig. 2. High resolution electron microscopy image of $Cu_{0.08}Zn_{0.92}O$ reduced in H_2.

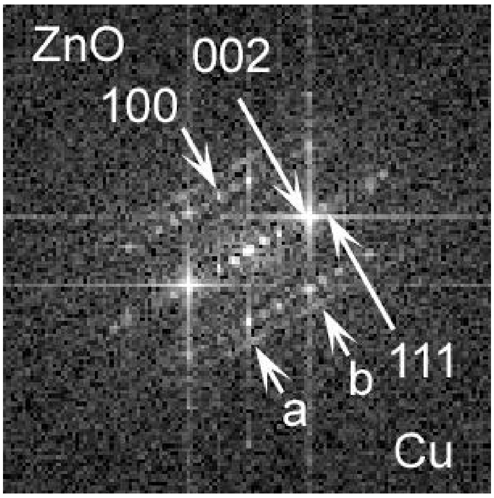

Fig. 3. Electron-diffraction $Cu_{0.08}Zn_{0.92}O$ reduced in H_2, indicating the coherence of the inclusion lattice and the main crystal.

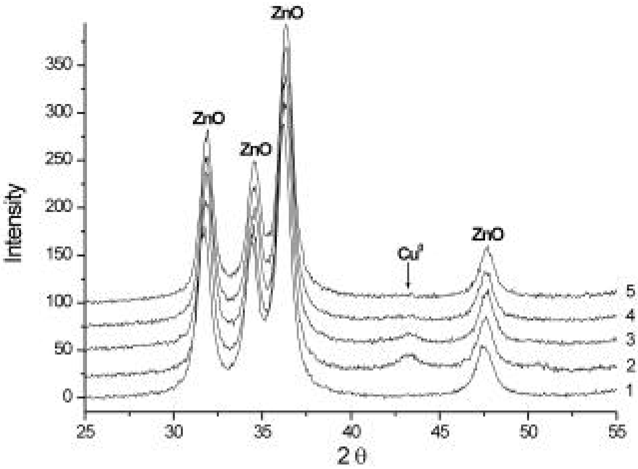

Fig. 4. In situ XRD patterns of $Cu_{0.08}Zn_{0.92}O$: (1) as prepared; (2) reduced in H_2; reoxidized in He + 0.05 vol% O_2 for (3) 1 h; (4) 2 h; (5) 3 h.

The observed reduction-oxidation reversibility of the main part of the copper from the solid solution without any accompanying change in the ZnO structure provides evidence for the following mechanisms:

- Reduction of Cu^{+2} ions occurs through their substitution by protons in the ZnO structure: $H_2 \leftrightarrow 2H$; $Cu^{+2} + 2H = Cu^0 + 2H^+$
- Oxidation occurs through the reaction of dissolved protons with O_2 from the gas phase, and electron transfer from the copper metal: $O_2 \leftrightarrow 2O$; $Cu^0+2H^+ + O = Cu^{+2} + H_2O$

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